termine the relative locations of the electrons which maximize the square of the determinant.[14] The problem with this approach is that the configuration which results depends on which orbitals are included in the determinant, just as the configuration of hybrid orbitals depends on which orbitals are hybridized. By means of group theory, appropriate orbitals can be chosen to generate *any* imagined symmetry for a given molecule.[15] As far as the Pauli principle is concerned, determinants giving unobserved configurations are as valid as the one giving the observed configuration. A classic example is the option of the d orbital in dsp^3, where the configuration is trigonal bipyramidal with d_{z^2} but square pyramidal with $d_{x^2-y^2}$. Attempts to justify the preference for d_{z^2} in terms of probability[14b] or Pauli forces[6c] are clearly incorrect.

Conclusion. For every conceivable shape of any molecule, a wave function can be written in compliance to the Pauli principle. From the infinity of such functions, the one representing the correct shape is not determined by the Pauli principle, which is equally satisfied by all of them. The Pauli principle is a necessary but not sufficient condition to the understanding of molecular shapes. The Pauli force is a misleading fiction that is as unjustified for explaining molecular shapes as it is for explaining Hund's rule.

Acknowledgment. We thank Dr. Russell T. Pack for suggesting the model of repulsion-free electrons, and for calling our attention to ref 2.

Supplementary Material Available. Tables IV-VI containing MO coefficients and energies for H_2O^{9+} will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6340.

References and Notes

(1) W. Kauzmann, "Quantum Chemistry: An Introduction", Academic Press, New York, N.Y., 1957, p 319 and 320; I. N. Levine, "Quantum Chemistry", Vol. I, Allyn and Bacon, Boston, Mass., 1970, p 305.

(2) J. Katriel, *Phys. Rev. A*, **5**, 1990 (1972).

(3) Y. Accad, C. L. Pekeris, and B. Schiff, *Phys. Rev. A*, **4**, 516 (1971).

(4) E. R. Davidson, *J. Chem. Phys.*, **41**, 656 (1964); **42**, 4199 (1965); A. Lemberger and R. Pauncz, *Acta Phys. Acad. Sci. Hung.*, **27**, 169 (1969); J. Katriel, *Theor. Chim. Acta*, **23**, 309 (1972); D. A. Kohl, *J. Chem. Phys.*, **56**, 4236 (1972).

(5) J. C. Slater, "Quantum Theory of Atomic Structure", Vol. I, McGraw-Hill, New York, N.Y., 1960, p 287 and 288; H. L. Strauss, "Quantum Mechanics: An Introduction", Prentice-Hall, Englewood Cliffs, N.J., 1968, p 168.

(6) (a) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963), *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967); (b) *J. Am. Chem. Soc.*, **82**, 5978 (1960); (c) *Can. J. Chem.*, **38**, 818 (1960).

(7) (a) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, **22**, 231 (1968); (b) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory", 2nd ed, Wiley, New York, N.Y., 1970, p 327 and 328; H. A. Bent, *J. Chem. Educ.*, **40**, 446 (1963); **45**, 768 (1968); L. C. Allen, *Theor. Chim. Acta*, **24**, 117 (1972).

(8) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(9) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

(10) See paragraph at end of paper regarding supplementary material.

(11) The Coulomb force between the nuclei is retained because without it a neon atom would be formed with an energy of −200 hartrees.

(12) L. Salem, *Proc. R. Soc. London, Ser. A*, **264**, 379 (1961).

(13) R. F. W. Bader and H. J. T. Preston, *Can. J. Chem.*, **44**, 1131 (1966).

(14) (a) H. K. Zimmerman, Jr., and P. Van Rysselberghe, *J. Chem. Phys.*, **17**, 598 (1949); J. E. Lennard-Jones, *ibid.*, **20**, 1024 (1952), *Adv. Sci.*, **11**, 136 (1954); A. Brickstock and J. A. Pople, *Philos. Mag.*, **44**, 705 (1953); (b) J. W. Linnett and C. E. Mellish, *Trans. Faraday Soc.*, **50**, 665 (1954). An instructive analogy to the error in logic in (b) regarding the likelihood of trigonal bipyramids is the patently false conclusion that the greater peak in the probability of flipping heads makes two-headed coins more likely than one-headed coins.

(15) F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed, Wiley, New York, N.Y., 1971, p 194–241.

Molecular Structure of Gaseous Hexachlorobutadiene

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Abstract: The molecular structure of hexachlorobutadiene has been investigated by electron diffraction from the vapor. The molecule is not coplanar anti as is butadiene itself at normal temperatures, but instead has a gauche conformation approximately midway between syn and anti corresponding to a rotation around the conjugated single bond. Assuming symmetry C_2, symmetric $C{=}CCl_2$ groups, and equal C-Cl bonds the important distance, r_a, and angle values were found to be $r_{C=C}$ = 1.349 (6) Å, r_{C-C} = 1.483 (18) Å, r_{C-Cl} = 1.715 (2) Å, ∠C=C—C = 123.4 (6)°. ∠C=C—Cl(terminal) = 122.5 (2)°, ∠C=C—Cl(central) = 122.0 (7)°, and θ (the CCCC dihedral angle relative to 0° for the anti form) = 101.9 (11)°; parenthesized values are 2σ and refer to the last digit given.

Based on interpretation of the Raman spectrum of hexachlorobutadiene, C_4Cl_6, Kohlrausch and Wittek[1] concluded that the molecule was noncoplanar, a result supported by their energy calculations which predicted a value of 98° for the angle of torsion about the central single bond (0° corresponds to the coplanar anti form). The noncoplanar structure of C_4Cl_6 was confirmed in 1953 by an ir study by Szasz and Sheppard.[2] Their low-temperature results also eliminated the possibility that the substance is a mixture of noncoplanar rotational isomers, and they judged the steric effects to be so great that one single minimum in the potential energy curve located in the near 90° position should be possible. Results from a new Raman investigation[3] and two uv studies[4,5] have been taken as further evidence against a coplanar anti conformation.

Butadiene[6,7] as well as many of the substituted butadienes[8] have been found to exist predominantly in the coplanar anti form at normal temperatures. The coexistence of a second conformer syn or gauche has been widely discussed but not conclusively verified.[9] Although high-temperature studies of butadiene[10] seem to indicate that a gauche conformer may be present, no second conformer has yet been observed for substituted butadienes for which the coplanar anti conformation has been established.[11-14] Sub-

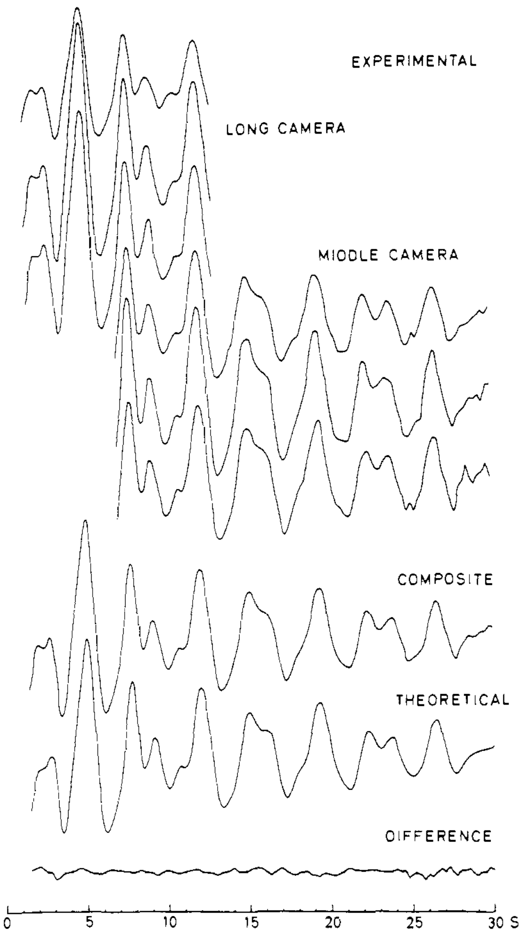

Figure 1. Intensity curves for hexachlorobutadiene. The long and middle camera curves and the composite curve are experimental. The theoretical curve was calculated from the parameter values of Table I.

stituted butadienes which, because of large 1,3 or 2,4 steric interactions, were believed to exist in skew forms[8,15] have so far been observed in only a gauche-like conformation.[12,15-17]

The observed shortening of carbon-carbon single bonds adjacent to multiple bonds has been a much studied subject. The shortening has been ascribed both to conjugation effects and to the hybridization state of the atoms involved. The facts that the double-bond lengths in butadienes are not significantly different from those in the corresponding ethylenes[7] and that the single-bond lengths do not seem to increase consistently with decreasing π-electron overlap[12] suggest that hybridization plays a more important role than conjugation.

This electron diffraction investigation, initiated at Oregon State University as a part of a study of conjugated systems, was carried out primarily to determine the conformation of the molecule. In addition it was hoped that the carbon-carbon bond lengths could be determined accurately enough to add information about the correlation between these bond lengths in butadienes and the amount of π-electron overlap.

Experimental and Data Reduction

The sample of hexachlorobutadiene was kindly provided by Dr. Robert Degeilh of Pechiney-Saint-Gobain and was used without further purification. Diffraction photographs were made in the OSU apparatus at nozzle-to-plate distances of 74.99 and 30.66 cm using an r^3 rotating sector, 8 × 10 in. Kodak projector slide (medium) plates, beam currents of 0.14–0.30 μA, and exposure times of 1–6 min. The nozzle-tip temperature was 100°C and the ambient pressure in the apparatus during sample run-in was about 6×10^{-6} Torr. The electron wavelengths were in the range 0.05718–0.05722 Å as calculated from the accelerating voltage accurately measured for each exposure and calibrated against diffraction patterns of gaseous CO_2.[18]

Three plates made at each of the two camera distances were selected for the structure analysis. The ranges of data from the longer and the shorter camera distances were respectively $1.00 \leq s \leq 13.00$ and $7.00 \leq s \leq 30.00$ ($s = 4\pi\lambda^{-1} \sin\theta$ where 2θ is the scattering angle), and the data interval was $\Delta s = 0.25$.

$I^E(s)$ curves were obtained from the distributions of the scattered intensity recorded on the plates by the usual procedure.[19,20] Further data processing and the structure analysis itself were carried out using the computer program system in Oslo.[21] The $I^E(s)$ curves[22] were therefore divided by the theoretical background to give the curves on a levelled form. Smooth backgrounds were subtracted and the resulting experimental molecular intensities were transformed to the modified form ($I_m^E(s)$) which has essentially constant coefficients and corresponds to

$$I_m^T(s) = \sum_{i,j} n_{ij} \frac{|f_i'(s)||f_j'(s)|}{|f_C'(s)||f_{Cl}'(s)|} \cos|\Delta\eta_{ij}| \times \sin(r_{ij}s)\exp(-\tfrac{1}{2}l_{ij}^2 s^2) \qquad (1)$$

where r is an interatomic distance, n the distance multiplicity, and l the root-mean-square amplitude of vibration. The scattering amplitudes, $|f_i|$ (proportional to $|f'(s)|/s^2$),[21] and the phases, η_i, used in this investigation were computed for 42 keV electrons by the partial wave approximation[23] using analytical expressions for the HF potentials for the carbon and chlorine atoms.[24] The modified molecular intensity curves obtained after computing radial distribution curves and redrawing the experimental backgrounds in the usual way so as to eliminate obvious errors are shown in Figure 1 together with the corresponding composite curve.[22] The indices of resolution were found to be 0.73 and 1.19 for the long and middle camera data, respectively.

Trial Structures

The experimental radial distribution curves were calculated from the composite modified curves according to

$$D(r) = \frac{2}{\pi}\Delta s \sum_{s_{\min}}^{s_{\max}} I_m^E(s)\exp(-Bs^2)\sin(rs) \qquad (2)$$

The final experimental radial distribution curve, shown in Figure 2, was calculated from the composite intensity curve in Figure 1, with data for the unobserved or uncertain inner region $0 \leq s \leq 1.25$ from the final model, $s_{\max} = 30.00$, and the artificial damping factor $B = 0.0015$.

The two first peaks of the radial distribution curve represent the bond distances and may be reproduced fairly well by the values $r_{C=C} = 1.35$ Å, $r_{C-C} = 1.50$ Å, $r_{C-Cl} = 1.715$ Å, $l_{C=C} = 0.042$ Å, $l_{C-C} = 0.045$ Å, and $l_{C-Cl} = 0.050$ Å. The most striking feature of the nonbonded part of the curve is the position of the longest distance peak at about 6.55 Å. This position virtually excludes the planar anti conformation which in a structure with roughly normal bond distances and bond angles should give a longest Cl···Cl distance in the vicinity of 6.75 Å. Since the planar syn structure is a priori unlikely for steric reasons, models of the molecule involving a twist about the conjugated carbon-carbon single bond (C_2 symmetry; see Figure 3) were indicated. Assuming coplanar $Cl_2C{=}C(Cl)$ groups and equally long terminal C-Cl bonds such models are described by nine geometrical parameters: two carbon-carbon and two carbon-chlorine bond distances, the four valence angles $\angle C{=}C{-}Cl_7$, $\angle C{=}C{-}Cl_9$, $\angle C{=}C{-}Cl_5$, and $\angle C{=}C{-}C$, and the angle of torsion about the C-C bond (θ). The peak at 2.7 Å clearly arises from the four types of C···Cl distances across a bond angle (2-7, 2-9, 1-5, 2-6). These four distance types must be nearly equal since the peak is relatively narrow; for example, assigning all geminal C···Cl distances the value 2.70 Å and amplitude $l = 0.07$ Å reprodu-

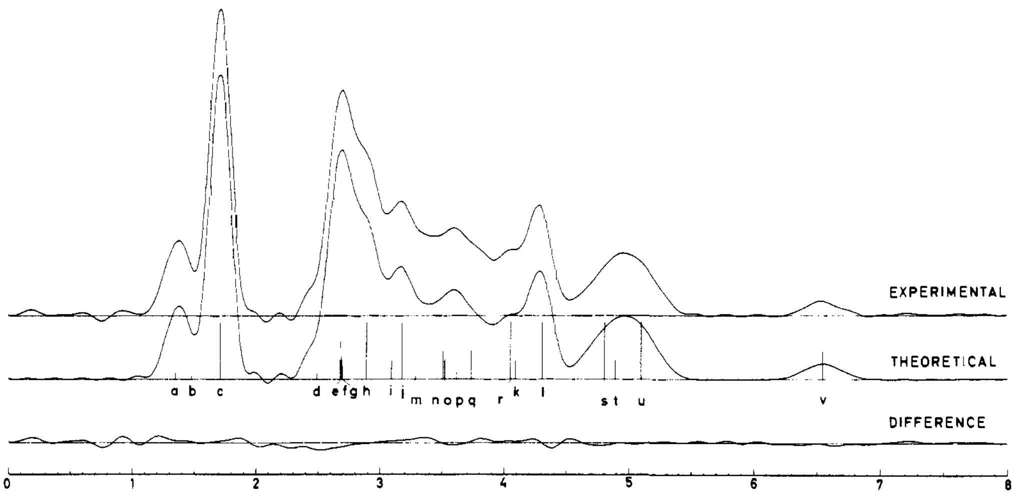

Figure 2. Radial distribution curve for hexachlorobutadiene. The curves were calculated from the composite and theoretical curves of Figure 1 with $B = 0.0015$. Unobserved experimental intensity data for the region $0 \leq s \leq 1.25$ were taken from the theoretical curve. The vertical lines indicate the interatomic distances of the final models: torsion-nonsensitive distances, (a) C═C, (b) C–C, (c) C–Cl, (d) $C_2 \cdots C_4$, (e) $C_1 \cdots Cl_5$, (f) $C_2 \cdots Cl_7$ and $C_2 \cdots Cl_9$, (g) $C_2 \cdots Cl_6$, (h) $Cl_7 \cdots Cl_9$, (i) $C_2 \cdots Cl_{10}$, (j) $Cl_5 \cdots Cl_7$, (k) $C_2 \cdots Cl_8$, (l) $Cl_5 \cdots Cl_9$; and torsion-sensitive distances (m) $C_1 \cdots C_4$, (n) $Cl_5 \cdots Cl_6$, (o) $C_1 \cdots Cl_{10}$, (p) $C_1 \cdots Cl_6$, (q) $Cl_9 \cdots Cl_{10}$, (r) $Cl_5 \cdots Cl_{10}$, (s) $Cl_7 \cdots Cl_{10}$, (t) $C_3 \cdots Cl_8$, (u) $Cl_5 \cdots Cl_8$, (v) $Cl_7 \cdots Cl_8$.

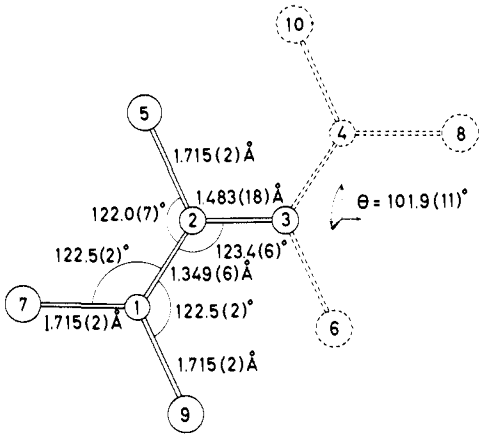

Figure 3. Atom numbering and final structure of gaseous hexachlorobutadiene; parenthesized values are 2σ and refer to the last digit given.

ces the peak quite well. Accordingly the assumption $\angle C{=}C{-}Cl_7 = \angle C{=}C{-}Cl_9$ was introduced. With these angles and $\angle C{=}C{-}Cl_5$ at 122.5° and with the bond lengths at the values mentioned above, torsion-independent distances are found at 4.3 Å ($Cl_5 \cdots Cl_9$) and 2.9 Å ($Cl_7 \cdots Cl_9$) in good agreement with peaks in the RD curve which then also suggest that the torsion-dependent C···Cl and Cl···Cl distances must be found at values greater than 3.4 Å. Calculations of the magnitudes of these as a function of torsion angle θ showed that values of θ greater than 110° and less than 70° ($\theta = 0$ corresponds to the coplanar anti form) gave Cl···Cl distances less than 3.4 Å, which is also substantially less than the van der Waals radius sum, and that a good fit to the remaining peaks of the RD curve would be given by values of θ near 100°.

Structure Refinement

The structure refinement was carried out by the method of least squares based upon intensity curves on the modified form described by eq 1, using the composite experimental intensity curve ($1.50 \leq s \leq 30.00$) and a diagonal weight matrix, the elements of which were calculated according to $w = \exp(-0.05(5 - s)^2)$ for $s < 5$, $w = 1$ for $5 \leq s \leq 28$, and $w = \exp(-0.016(s - 28)^2)$ for $s > 28$ Å^{-1}.[21]

A preliminary refinement with all C–Cl bonds equal and where most of the amplitudes of vibration for the nonbonded interactions were kept fixed at values obtained from the analysis of the RD curve was carried out. The resulting amplitudes of vibration for the carbon–carbon distances ($l_{C=C} = 0.0506$ (64) Å and $l_{C\text{-}C} = 0.0571$ (162) Å) were considered unreasonably large and that for the C–Cl interaction ($l_{C\text{-}Cl} = 0.0534$ (10) Å) somewhat too large. The large standard errors associated with the carbon–carbon amplitudes suggested that the geometrical parameter values would be insensitive to small changes in the amplitudes and accordingly they were given the more reasonable values $l_{C=C} = 0.042$ Å and $l_{C\text{-}C} = 0.048$ Å. The somewhat large amplitude for the C–Cl bond was, however, more disturbing. Although the C–Cl peak did not seem to feature any clear asymmetry caused by a possible two to one splitting of the distance, it was felt necessary to investigate the influence of a small C–Cl split upon the other structural parameters. As expected, subsequent refinements showed that the C–C bond was extremely sensitive to the values of the split as well as to the value of the C–Cl amplitude. However, the least-squares fit was substantially poorer when split was introduced and the C–Cl amplitude remained large for all reasonable values of the split. The restriction of C–Cl(terminal) = C–Cl(central) thus seemed to be justified, which reduced the number of geometrical parameters to seven.

The structure determination was continued with a search for the best set of amplitudes for the nonbonded interactions. Because many of the distances overlapped this could not be done by refinement of all the parameters simultaneously. The following two restraints were used in all the refinements: $l_{C_1 \cdots Cl_7} = l_{C_3 \cdots Cl_5} = l_{C_1 \cdots Cl_6}$ were refined as a group and $l_{C_1 \cdots C_4}$ and $l_{C_3 \cdots C_4}$ were kept fixed at the values 0.07 and 0.08 Å, respectively, since the carbon···carbon distances contribute very little to the scattered intensity. Of the remaining amplitudes six belong to distances that do not overlap much with others and these were allowed to refine freely. The last eight amplitudes, however, were highly correlated in four pairs ($C_2 \cdots Cl_8/Cl_5 \cdots Cl_{10}$, $C_1 \cdots Cl_6/Cl_9 \cdots Cl_{10}$, $C_1 \cdots Cl_8/Cl_7 \cdots Cl_{10}$, and $C_1 \cdots Cl_{10}/Cl_5 \cdots Cl_6$), and simultaneous refinements of these proved impossible. Alternating refinement of the four C···Cl and four Cl···Cl amplitudes was therefore carried out together with the refinement of the other amplitudes and geometrical parameters. The paired amplitudes showed a tendency to refine to one smaller and one larger value. The refinement was therefore repeated now keeping these amplitudes at reasonable values. The least-squares fit was only slightly poorer and the resulting parameter values did not change significantly. The results from this refinement are given in Table I. The estimated standard errors are obtained from the relations

$$2\sigma_r = 2[2\sigma_{LS}^2 + (0.0005r)^2]^{1/2}$$

$$2\sigma_l = 2[2\sigma_{LS}^2 + (0.02l)^2]^{1/2}$$

$$2\sigma_{angle} = 2[2\sigma_{LS}^2]^{1/2} \qquad (3)$$

Table I. Final Parameter Values[a,b] for Hexachlorobutadiene

Parameter[c]	r_a	l_a[f]
C=C	1.349 (6)	[0.042]
C—C	1.483 (18)	[0.048]
C—Cl	1.715 (2)	0.053 (3)
$C_2 \cdots Cl_7$	2.692 (5)	0.069 } (4)
$C_1 \cdots Cl_5$	2.686 (10)	0.069 } (4)
$C_2 \cdots Cl_6$	2.693 (13)	0.069 } (4)
$C_2 \cdots Cl_8$	4.091 (16)	[0.10]
$C_2 \cdots Cl_{10}$	3.094 (16)	0.083 (22)
$Cl_5 \cdots Cl_7$	3.179 (15)	0.126 (14)
$Cl_5 \cdots Cl_9$	4.304 (7)	0.073 (7)
$Cl_7 \cdots Cl_9$	2.893 (7)	0.066 (5)
$C_2 \cdots C_4$	2.494 (17)	[0.07]
$C_1 \cdots C_4'$	3.290 (23)	[0.08]
$C_1 \cdots Cl_6'$	3.614 (16)	[0.15]
$C_1 \cdots Cl_8'$	4.889 (22)	[0.15]
$C_1 \cdots Cl_{10}'$	3.523 (26)	[0.15]
$Cl_5 \cdots Cl_6'$	3.510 (25)	[0.15]
$Cl_5 \cdots Cl_8'$	5.099 (15)	0.157 (23)
$Cl_5 \cdots Cl_{10}'$	4.053 (29)	[0.20]
$Cl_7 \cdots Cl_8'$	6.546 (22)	0.148 (55)
$Cl_7 \cdots Cl_{10}'$	4.807 (30)	[0.20]
$Cl_9 \cdots Cl_{10}'$	3.737 (35)	0.152 (50)
∠C=C—Cl_7	122.5 (2)	
∠C=C—Cl_5	122.0 (7)	
∠C=C—C	123.4 (6)	
∠θ[d]	101.9 (11)	
R[e]	0.070	

[a] Distances, r_a, and root-mean-square amplitudes, l_a, in ångströms; angles in degrees. [b] Parenthesized values are 2σ and include estimates of systematic errors. They refer to the last digit given. [c] See Figure 3 for the atomic numbering. Primed items refer to torsion-sensitive distances. [d] The CCCC dihedral angle relative to 0° for the anti conformation. [e] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i I_i^2(\text{obsd})]^{1/2}$ where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$. [f] Amplitudes in braces were refined as a group; amplitudes in brackets were assumed.

where the factor 2 accounts for possible correlation among the data and the factors 0.0005 and 0.02 take systematic errors into account. σ_{LS}^2 are the diagonal elements σ_{ii}^2 of the error matrix $\{\rho_{ij}\sigma_i\sigma_j\}$ obtained from the least-squares refinement. The ρ_{ij} matrix reflects the correlation among the parameters and is given in Table II. Theoretical intensity and radial distribution curves were calculated according to the parameter values of Table I and are shown in Figures 1 and 2, respectively, together with the corresponding experimental and difference curves. The difference curves and the R factor (7%) demonstrate that the agreement between the resulting model and the experimental data is good, and possible coexistence of other conformers was ruled out.

Discussion

Hexachlorobutadiene is found to be in a syn-twisted conformation with a CCCC dihedral angle of 101.9 (11)°, i.e., not far from the 98 and 90° suggested by the earlier investigators.[1,2] That the molecule is twisted is clear from molecular models which show considerable steric strain in the coplanar forms, a strain which as far as the van der Waals repulsions between the chlorine atoms is concerned is relieved for dihedral angles greater than 78° and less than 98°. As to why a syn-twisted conformation is preferred over an anti-twisted one is presently not quite understood.[9] However, this result confirms the conformations found for other substituted butadienes which display large 1,3 or 2,4 steric repulsions, as the dihedral angles for derivatives with such F,F, CH_3,CH_3, and CH_3,CH_2OH interactions are found to be 137.6 (6)°,[16] 113.3 (20)° and 114.3 (13)°,[12] and 104.8 (4)°,[17] respectively. The conformation of hexachlorobutadiene is found to be slightly closer to the syn form than what was expected from van der Waals repulsion between the chlorine atoms as one Cl···Cl distance ($r_{Cl_5 \cdots Cl_6}$ = 3.510 (25) Å) appears to be significantly shorter than the van der

Table II. Correlation Matrix for Parameters of Hexachlorobutadiene[a]

	$r_{C=C}$	r_{C-Cl}	r_{C-C}	∠C=C—Cl_7	∠C=C—Cl_5	∠C=C—C	θ	l_{C-Cl}	$l_{3,7}$	$l_{2,10}$	$l_{5,7}$	$l_{5,9}$	$l_{7,9}$	$l_{5,8}$	$l_{7,8}$	$l_{9,10}$	Scale
σ[b]	0.0021	0.0063	0.0006	0.074	0.253	0.210	0.386	0.0009	0.0011	0.0078	0.0046	0.0022	0.0016	0.0093	0.0195	0.0142	0.224
	1.00	−0.06	−0.25	−0.48	−0.14	0.27	0.14	−0.05	0.08	−0.14	0.06	0.02	−0.12	0.18	0.00	0.04	−0.09
		1.00	−0.18	−0.60	0.65	−0.31	−0.33	−0.35	−0.01	−0.39	−0.15	−0.06	−0.34	0.14	−0.01	0.29	−0.19
			1.00	0.40	−0.25	0.27	0.11	0.08	0.05	0.05	0.13	0.05	0.07	0.07	0.00	−0.02	0.06
				1.00	−0.57	0.25	0.24	0.16	−0.21	0.37	0.29	0.03	0.26	−0.09	0.00	−0.16	0.01
					1.00	−0.60	−0.44	−0.12	0.14	−0.54	−0.26	−0.06	−0.28	−0.06	0.00	0.01	0.07
						1.00	0.44	0.00	−0.05	0.22	0.46	0.09	0.23	0.31	0.00	−0.14	−0.13
							1.00	0.05	−0.06	0.16	0.24	0.09	0.13	−0.03	0.00	−0.36	−0.06
								1.00	0.27	0.12	−0.02	0.10	0.23	−0.05	0.03	−0.12	0.62
									1.00	−0.01	−0.14	0.08	0.27	0.02	0.02	−0.03	0.41
										1.00	−0.11	0.04	0.49	−0.04	0.00	0.01	0.00
											1.00	0.04	0.09	0.14	0.00	−0.21	−0.09
												1.00	0.08	0.03	0.01	−0.08	0.17
													1.00	0.00	0.01	−0.11	0.19
														1.00	0.00	0.07	−0.03
															1.00	0.00	0.05
																1.00	−0.09
																	1.00

[a] Distances, r, and root-mean-square amplitudes, l, in ångströms. [b] Standard deviations from least squares.

Waals radius sum of 3.6 Å. A similar tendency is, however, also found in 2,2′-dihalobiphenyls which are found in conformations with the two halogens on the same side and except for the fluorine compound with the halogen–halogen distances shorter than the van der Waals distances.[9]

The bond angles around the central and terminal carbon atoms do not differ much which to the extent one can assume that bonds are not bent indicates that the hybridization states of the two types of carbons are quite similar. This supports the experimentally founded assumption that the central and terminal C–Cl bonds are equally long, an assumption which seems to be further justified by the molecular structure of *cis,cis*-1,2,3,4-tetrachlorobutadiene.[13] As determined from X-ray data the bond angles of this compound ($\angle C{=}C{-}C$ = 121.7 (10)°, $\angle C{=}C{-}Cl$(terminal) = 121.3 (8)°, and $\angle C{=}C{-}Cl$(central) = 122.0 (8)°) agree well with the corresponding ones in hexachlorobutadiene, and the C–Cl bond distances ($r_{\mathrm{C-Cl(terminal)}}$ = 1.715 (11) Å and $r_{\mathrm{C-Cl(central)}}$ = 1.701 (12) Å) are not found to differ significantly and they confirm to the value found for this bond in hexachlorobutadiene (1.715 (2) Å).

The structures of the chlorinated vinyl groups in hexachlorobutadiene and tetrachloroethylene are not significantly different, the structural parameters of the latter being $r_{\mathrm{C=C}}$ = 1.354 (3) Å; $r_{\mathrm{C-Cl}}$ = 1.718 (3) Å, and $\angle C{=}C{-}Cl$ = 122.4 (3)°.[25] Since there is a minimal π-electron overlap in hexachlorobutadiene this is not surprising as is, in terms of the conjugation theory, the apparent equal vinyl groups in butadiene and ethylene.[7] Unfortunately, the determination of the carbon–carbon single bond is associated with large error limits which make significant trends in the variation of this bond distance as a function of the CCCC dihedral angle difficult to deduce. This task is also complicated by different effects from the substituents and possible changes in the hybridization state of the atoms involved. The π-electron overlap in hexachlorobutadiene is, however, close to its minimum and the observed C–C distance of 1.483 (18) Å should be practically free from conjugation. *cis,cis*-1,2,3,4-Tetrachlorobutadiene appears to be a well-suited anti-planar reference molecule since the substituents as well as the valence angles of the carbon atoms involved are similar. The C–C single bond in this molecule, where the π-electron overlap has a maximum, is 1.492 (11) Å. These results therefore indicate, as do the result for the tetramethyl derivatives of butadiene,[12] that the length of the C–C single bond in butadienes is only minimally affected by the degree of π-electron overlap. By choosing 2,3-dichlorobutadiene[14] as the anti-planar reference molecule one may be led to moderate this conclusion somewhat. However, the long C–Cl bond distance (1.747 (3) Å) and the large angle opposite this bond ($\angle C{=}C{-}C$ = 126.9 (2)°) suggest that the bonding conditions in this molecule are different. The large $\angle C{=}C{-}C$ angle indicates that the central carbon atom deviates from sp^2 hybridization in such a manner as to reduce the s character of the C–Cl bond which is in accordance with the relatively long distance observed. The somewhat short C–C distance in this molecule may then be correlated to the relatively large deviation from sp^2 hybridization of the carbon atoms and this result may then rather be used to support the statement that hybridization is more important than conjugation as far as the bond lengths in conjugated systems are concerned.

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Supplementary Material Available. The intensity data, separate $I^{\mathrm{E}}(s)$ curves, and composite molecular intensity curves on the modified form, $I_{\mathrm{m}}{}^{\mathrm{E}}(s)$, and on the form which corresponds to $I_{\mathrm{m}}{}^{\mathrm{E}}(s)|f_{\mathrm{C}}'(s)||f_{\mathrm{Cl}}'(s)|$ (cf. eq 1) will appear immediately following this article in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6342.

References and Notes

(1) K. W. F. Kohlrausch and H. Wittek, *Chem. Ber.*, **75**, 227 (1942).
(2) G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).
(3) M. I. Batuev and A. D. Matveeva, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1393 (1958).
(4) A. Roedig and R. Kloss, *Justus Liebigs Ann. Chem.*, **612**, 1 (1958).
(5) E. Rutner and S. H. Bauer, *J. Chem. Phys.*, **68**, 1768 (1964).
(6) W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966).
(7) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).
(8) A. A. Bothner-By and D. Jung, *J. Am. Chem. Soc.*, **90**, 2342 (1968), and references therein.
(9) O. Bastiansen, H. M. Seip, and J. Boggs, "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N.Y., 1971, pp 60–165.
(10) O. Bastiansen, G. Hagen, and M. Traetteberg, unpublished work.
(11) C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968).
(12) M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970); Ph.D. Thesis, University of Trondheim, Trondheim, Norway, 1969.
(13) Y. Otaka, *Acta Crystallogr., Sect. B*, **28**, 342 (1972).
(14) J. A. Neisess, G. Gundersen, and K. Hedberg, in preparation for publication.
(15) A. A. Bothner-By and D. F. Koster, *J. Am. Chem. Soc.*, **90**, 2351 (1968).
(16) C. H. Chang, A. L. Andreassen, and S. H. Bauer, *J. Org. Chem.*, **36**, 920 (1971).
(17) T. Ottersen, L. W. Jelinski, E. F. Kiefer, and K. Seff, *Acta Crystallogr., Sect. B*, **30**, 960 (1974).
(18) r_{a}(C—O) = 1.1640 Å, r_{a}(O···O) = 2.3244 Å: K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **40**, 505 (1967).
(19) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1970).
(20) K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).
(21) B. Andersen, H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, **23**, 3224 (1969).
(22) See paragraph at end of paper regarding supplementary material.
(23) J. L. Peacher and J. C. Wells, *J. Chem. Phys.*, **46**, 4809 (1967).
(24) T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, **40**, 1686 (1964).
(25) T. G. Strand, *Acta Chem. Scand.*, **21**, 2112 (1967).