pare the solutions of reactant leuconitrile to match the absorption of the actinometer solution or to prepare solutions (ca. 3×10^{-3} M) that were opaque (OD > 2) over the wavelengths at which the light source was emitting. All the solutions in each run were opaque (<0.1% T) at 313 nm where the light source emitted 74.9% of its light. In this manner, the solutions in each run absorbed the same amount of light.

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Dodecachlorotetracyclo[7.2.1.$0^{2,8}$.$0^{5,12}$]dodeca-3,6,10-triene, a Fully Chlorinated Valence Isomer of [12]Annulene

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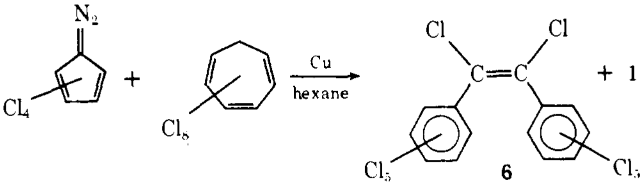
Abstract: The title compound (**1**), representing a new tetracyclic ring system, has been synthesized from tetrachlorodiazocyclopentadiene and octachlorocycloheptatriene. The structure of **1** was established by single crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with a = 14.655 (5) Å, b = 16.874 (5) Å, c = 7.637 (1) Å, α = 100.43 (2)°, β = 102.19 (2)°, γ = 89.89 (2)°, V = 1814.0 (8) Å^3, and Z = 4. Data were collected on an autodiffractometer and refined with anisotropic least-squares to a final unweighted R value of 3.2%. When **1** is heated with copper, it is converted to perchloroacenaphthylene.

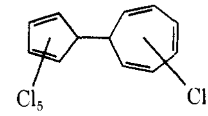
Complete substitution with chlorine is known to confer stability on otherwise rather unstable hydrocarbons.[1] In an attempt to synthesize a precursor to perchloropentaheptafulvalene, we have inadvertently synthesized dodecachlorotetracyclo[7.2.1.$0^{2,8}$.$0^{5,12}$]dodeca-3,6,10-triene (**1**), the first example of a new tetracyclic ring system.[2] Compound **1** is a stable, fully chlorinated valence isomer of [12]annulene.[3]

The reaction of tetrachlorodiazocyclopentadiene[4] with octachlorocycloheptatriene[5] in the presence of finely divided copper afforded two $C_{12}Cl_{12}$ compounds in about a 2:5 ratio for a total yield of 70–75%. The rather insoluble minor component was identified as perchloro-*cis*-stilbene (**6**) by comparison of its infrared spectrum with that of an authentic sample.[6]

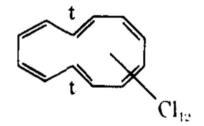
The major component **1** was a white solid soluble in organic solvents, showing two olefinic absorptions in the infrared at 1625 and 1585 cm^{-1} ($CHCl_3$ solution). The spectrum in chloroform showed little change in position or intensity of the olefinic absorptions between −50 and +50°C, suggesting that a temperature-dependent equilibrium of valence isomers was absent and that only one isomer was involved. The ultraviolet spectrum showed only a single absorption at 226 nm (log ϵ 3.76), thereby excluding conjugated structures such as **2** or **3**.



6



2

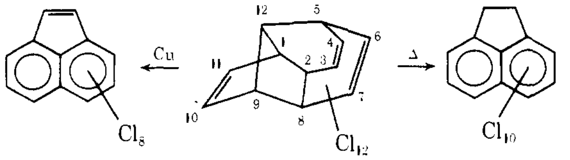


3

(+ isomers)

A room-temperature NQR spectrum of **1** exhibited ten different resonances, two of which had doubled intensity. The spectral spread was between 37.30 and 40.46 MHz with six absorptions between 38.33 and 40.46 MHz, a region in which chlorines attached to saturated carbons absorb.[7,8]

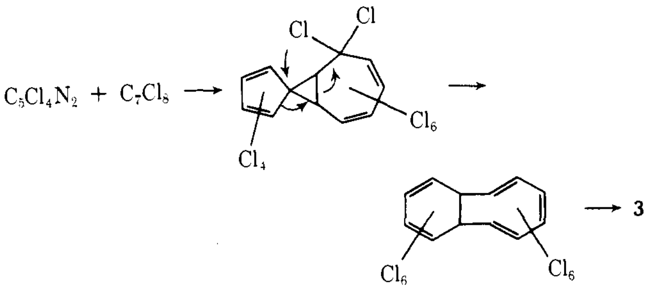
When **1** was heated with finely divided copper or with triethyl phosphite, an orange-red solid precipitated which was identified as perchloroacenaphthylene (**4**).[9] Thermolysis of **1** for 20 min at 200° afforded a mixture of products, not all of which have yet been characterized. One of the products, isolated in 28% yield, was identified as perchloroacenaphthene (**5**).[9] The NQR and uv spectra along with the formation of **4** and **5** suggested the following formula for **1**:



4 **1** **5**

Cleavage of the C_2-C_8 bond would allow an easy entry into the acenaphthene system.

However, a ^{13}C NMR study of **1** was in apparent disagreement with the assigned structure.[10] Only three resonances were observed, all in the olefinic region at 56.1, 58.3, and 63.0 ppm upfield from external carbon disulfide. A reexamination of the spectrum in tetrachloroethylene did not reveal any saturated carbon resonances. This observation suggested structure **3** which could conceivably arise as follows:



While this structure would explain the ^{13}C spectrum, the formation of **4** and **5** is not easily visualized as **3** would reasonably be expected to give perchlorobiphenylene on dechlorination.

At this point, an X-ray crystallographic study was undertaken to resolve the structural question. The result, shown in Figure 1, unambiguously confirms the structure of **1** as postulated above. The crystal structure contains two independent molecules of $C_{12}Cl_{12}$ in the unit cell. Bond lengths and angles for each molecule are given in Tables I and II, and these parameters for the two molecules agree to within three standard deviations.

As a result of the highly rigid carbon skeleton, each molecule possesses a pseudo-mirror plane along the C(5)-C(12) bond, bisecting the C(10)-C(11) bond, as seen in Figure 1. From inspection of Tables I and II, it can be seen that this symmetry is obeyed to within one or two standard deviations with the exception of C(4)-C(5) and C(5)-C(6) which are within 3σ.

The bond lengths and angles show the localization of the double bonds in the expected positions in **1**. The large variations in carbon-chlorine bond lengths are compatible with the different hybridizations on the carbon atoms. Two exceptionally long C-C distances of 1.674 (6) Å between C(2) and C(8) and 1.615 (6) Å between C(5) and C(12) can be rationalized in light of the strained tetracyclic carbon framework. The molecular parameters appear to be little affected by crystal packing forces, as there are no intermolecular distances less than 3.35 Å.

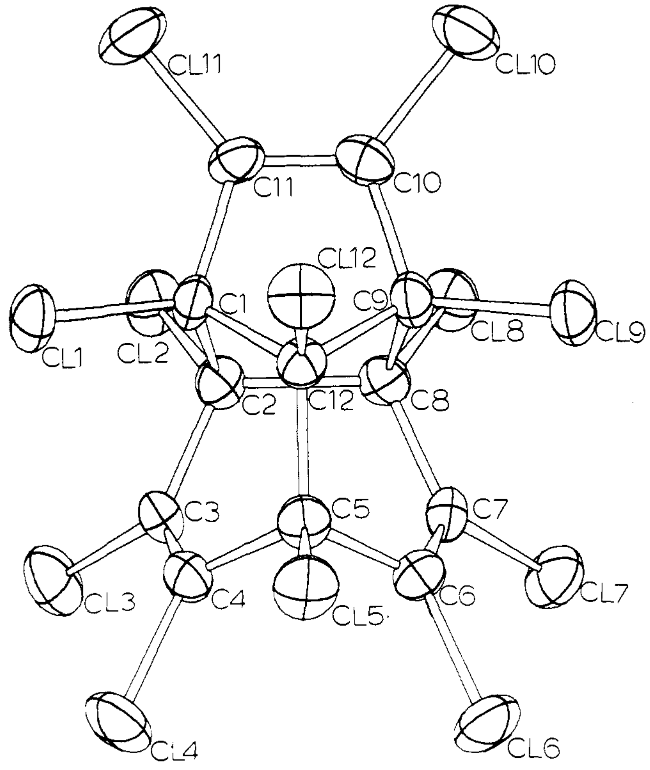


Figure 1. A drawing of a molecule of compound **1**. The 30% probability thermal ellipsoids are shown.

The most likely explanation for the lack of saturated carbon resonances in the ^{13}C NMR spectrum of **1** is that the saturated carbon atoms have a long spin-lattice relaxation time (T_1) combined with a very short spin-spin relaxation time (T_2). The latter is significant for carbons attached to quadrupolar nuclei.[11] In addition, with no protons present, the Overhauser enhancement associated with proton decoupling is not observed.

The photolysis of substituted diazocyclopentadienes with cycloheptatriene has been reported to yield spirohomonorcaradienes and pentaheptafulvalenes.[12] The abstraction of a chlorine atom from carbon tetrachloride under photolytic conditions to give 5-trichloromethylpentachlorocyclopentadiene has also been reported.[13] A possible explanation for the insertion reaction leading to the formation of **1** involves the initial abstraction of a chlorine atom from C_7Cl_8 to form a pentaheptafulvalene followed by an internal Diels-Alder reaction under the reaction conditions. Attempts to isolate this intermediate by arresting the reaction after 20% completion afforded small amounts of **1** and **6** and no other identifiable products except starting materials.

Another example of this tetracyclic ring system has recently been reported by Moberg and Nilsson.[14] The reaction of nickelocene with octachlorocycloheptatriene afforded 2,3,4,5,6,7,8-heptachlorotetracyclo[$7.1.2.0^{2,8}.0^{5,12}$]dodeca-3,6,10-triene (**7**), identical with **1** except for the substitution of hydrogen atoms for chlorine atoms at positions 1, 9, 10, 11, and 12. Compounds **7** and **1** have almost identical uv spectra. Similar to our results with **1**, Moberg and Nilsson report difficulty in determining ^{13}C NMR for the carbon atoms bound to chlorine in **7**. Frequencies were reported nly for the carbons bound to hydrogen.

Table I. Interatomic Distances for Compound 1, Å[a]

	Molecule 1	Molecule 2
C(1)–C(2)	1.576 (6)	1.561 (6)
C(1)–C(11)	1.514 (6)	1.505 (6)
C(1)–C(12)	1.550 (5)	1.563 (6)
C(2)–C(3)	1.510 (6)	1.514 (6)
C(2)–C(8)	1.674 (6)	1.678 (6)
C(3)–C(4)	1.322 (6)	1.326 (6)
C(4)–C(5)	1.545 (6)	1.529 (6)
C(5)–C(6)	1.526 (6)	1.532 (6)
C(5)–C(12)	1.615 (6)	1.613 (6)
C(6)–C(7)	1.333 (6)	1.327 (6)
C(7)–C(8)	1.517 (6)	1.522 (6)
C(8)–C(9)	1.578 (6)	1.566 (6)
C(9)–C(10)	1.503 (6)	1.511 (6)
C(9)–C(12)	1.561 (6)	1.562 (6)
C(10)–C(11)	1.313 (6)	1.308 (6)
Cl(1)–C(1)	1.762 (4)	1.758 (4)
Cl(2)–C(2)	1.758 (4)	1.766 (4)
Cl(3)–C(3)	1.707 (4)	1.715 (4)
Cl(4)–C(4)	1.709 (4)	1.707 (4)
Cl(5)–C(5)	1.774 (4)	1.771 (4)
Cl(6)–C(6)	1.710 (4)	1.705 (4)
Cl(7)–C(7)	1.713 (4)	1.711 (4)
Cl(8)–C(8)	1.759 (4)	1.764 (4)
Cl(9)–C(9)	1.759 (4)	1.761 (4)
Cl(10)–C(10)	1.701 (4)	1.706 (4)
Cl(11)–C(11)	1.697 (4)	1.708 (4)
Cl(12)–C(12)	1.760 (4)	1.762 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables.

Table II. Intermolecular Angles for Compound **1**, Deg

	Molecule 1	Molecule 2
Cl(1)–C(1)–C(2)	114.3 (3)	114.9 (3)
Cl(1)–C(1)–C(11)	113.9 (3)	113.2 (3)
Cl(1)–C(1)–C(12)	116.1 (3)	116.4 (3)
C(2)–C(1)–C(11)	109.3 (3)	109.4 (3)
C(2)–C(1)–C(12)	98.3 (3)	98.2 (3)
C(11)–C(1)–C(12)	103.3 (3)	103.3 (3)
Cl(2)–C(2)–C(1)	111.1 (3)	111.5 (3)
Cl(2)–C(2)–C(3)	112.3 (3)	111.7 (3)
Cl(2)–C(2)–C(8)	112.6 (3)	112.6 (3)
C(1)–C(2)–C(3)	105.7 (3)	105.5 (3)
C(1)–C(2)–C(8)	99.9 (3)	100.1 (3)
C(3)–C(2)–C(8)	114.3 (3)	114.7 (3)
Cl(3)–C(3)–C(2)	120.1 (3)	121.0 (3)
Cl(3)–C(3)–C(4)	122.3 (3)	121.7 (3)
C(2)–C(3)–C(4)	117.3 (4)	116.9 (4)
Cl(4)–C(4)–C(3)	123.2 (3)	122.9 (4)
Cl(4)–C(4)–C(5)	119.1 (3)	118.8 (3)
C(3)–C(4)–C(5)	116.8 (4)	117.3 (4)
Cl(5)–C(5)–C(4)	111.1 (3)	111.0 (3)
Cl(5)–C(5)–C(6)	111.0 (3)	111.2 (3)
Cl(5)–C(5)–C(12)	111.3 (3)	110.8 (3)
C(4)–C(5)–C(6)	100.3 (3)	100.8 (3)
C(4)–C(5)–C(12)	110.7 (3)	111.1 (3)
C(6)–C(5)–C(12)	112.0 (3)	111.5 (3)
Cl(6)–C(6)–C(5)	119.3 (3)	119.3 (3)
Cl(6)–C(6)–C(7)	122.3 (3)	122.5 (3)
C(5)–C(6)–C(7)	117.4 (4)	117.2 (4)
Cl(7)–C(7)–C(6)	122.9 (3)	122.9 (3)
Cl(7)–C(7)–C(8)	120.4 (3)	120.3 (3)
C(6)–C(7)–C(8)	116.6 (4)	116.7 (4)
Cl(8)–C(8)–C(2)	112.8 (3)	112.6 (3)
Cl(8)–C(8)–C(7)	111.8 (3)	112.2 (3)
Cl(8)–C(8)–C(9)	111.1 (3)	110.6 (3)
C(2)–C(8)–C(7)	114.1 (3)	114.2 (3)
C(2)–C(8)–C(9)	100.7 (3)	100.6 (3)
C(7)–C(8)–C(9)	105.5 (3)	105.8 (3)
Cl(9)–C(9)–C(8)	114.9 (3)	114.7 (3)
Cl(9)–C(9)–C(10)	114.0 (3)	114.0 (3)
Cl(9)–C(9)–C(12)	116.3 (3)	116.3 (3)
C(8)–C(9)–C(10)	109,2 (3)	109.7 (3)
C(8)–C(9)–C(12)	97.7 (3)	97.8 (3)
C(10)–C(9)–C(12)	103.0 (3)	102.8 (3)
Cl(10)–C(10)–C(9)	124.0 (3)	123.6 (3)
Cl(10)–C(10)–C(11)	127.5 (3)	128.3 (4)
C(9)–C(10)–C(11)	108.2 (4)	107.9 (4)
Cl(11)–C(11)–C(1)	123.4 (3)	123.4 (3)
Cl(11)–C(11)–C(10)	128.9 (3)	128.2 (3)
C(1)–C(11)–C(10)	107.6 (4)	108.1 (4)
Cl(12)–C(12)–C(1)	111.9 (3)	111.6 (3)
Cl(12)–C(12)–C(5)	113.3 (3)	114.0 (3)
Cl(12)–C(12)–C(9)	111.4 (3)	111.2 (3)
C(1)–C(12)–C(5)	113.6 (3)	113.1 (3)
C(1)–C(12)–C(9)	92.0 (3)	91.6 (3)
C(5)–C(12)–C(9)	112.8 (3)	113.3 (3)

Experimental Section

General. Melting points are uncorrected. Infrared spectra were obtained in $CHCl_3$ or as mulls on Perkin-Elmer Model 237 and 437 recording spectrophotometers. Ultraviolet spectra were recorded in *n*-pentane on a Cary Model 14 spectrophotometer. Room-temperature nuclear quadrupole resonance spectra were obtained on a Wilks NQR-1A commercial spectrometer and low-temperature spectra on a Decca-Radar spectrometer. Elemental analysis were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of 1. In a 100-ml round-bottomed flask provided with a magnetic stirrer and condenser was placed 4.6 g (0.02 mol) of tetrachlorodiazocyclopentadiene,[4] 7.36 g (0.02 mol) of octachlorocycloheptatriene,[5] and 4.0 g of finely divided (electrolytic grade) copper. The flask was purged with nitrogen followed by 40 ml of *n*-hexane. The top of the condenser was attached to a gas bubbler. The slurry was stirred and heated at 40–45°. Nitrogen gas was evolved slowly, and the contents of the flask became brownish. Nitrogen evolution was complete in about 16 hr. The brown slurry was stirred for an additional 4 hr at this temperature and filtered. The grey-brown insoluble residue remaining on the filter was washed with three 20-ml portions of hot *n*-hexane and dried (8.7 g). The filtrate and washings were combined and evaporated to dryness in vacuum to give 7.1 g of a brownish sticky solid which was washed with 20 ml of hot acetonitrile to remove most of the colored impurities. The pale buff-colored solid, 6.2 g (51.8%), was dissolved in 50 ml of *n*-hexane, boiled with decolorizing carbon, and filtered, and the solution was concentrated to 30 ml and cooled to give 4.4 g of colorless crystals. An analytical sample was prepared by recrystallization from *n*-hexane: mp 197–200° (rearrangement and decomposition); uv (pentane) λ_{max} 226 mμ (log ϵ 3.76); ir (mull, CsI) 1622 (s) 1582 (s), 1190 (s), 1169 (m), 1140 (ms), 1098 (wm), 1075 (m), 1058 (wm), 1033 (m), 970 (s), 910 (m), 820 (w), 775 (w), 752 (w), 722 (wm), 678 (s), 646 (s), and 600 (s) ±5 cm^{-1}; NQR (300 K) (Wilks) 37.30 (1), 37.43 (2), 37.72 (2), 37.96 (1), 38.33 (1), 38.55 (1), 39.31 (1), 39.65 (1), 40.24 (1), and 40.46 (1) ±0.05 MHz; NQR (77 K) (Decca Radar) 37.5–38.3 (12), 38.54 (1), 38.64 (1), 38.90 (1), 38.94 (1), 39.61 (1), 39.66 (1), 39.76 (1), 39.81 (1), 40.12 (2), 40.68 (1), and 40.92 (1) ±0.01 MHz.

Anal. Calcd for $C_{12}Cl_{12}$: C, 25.31; Cl, 74.69. Found: C, 25.47; Cl, 74.53.

The residue on top of the filter containing copper was extracted with 200 ml of hot benzene and filtered. The benzene solution was evaporated to dryness under vacuum. A white residue (1.3 g) was left behind, whose spectral characteristics were identical with those of an authentic sample of perchloro-*cis*-stilbene.[6] Additional amounts of this material could be obtained by repeated extraction of the copper-contaminated residue. The total yield was 18–20%.

High-Pressure Hydrogenation of 1. A 3-g sample of **1** was mixed with an equivalent amount of anhydrous sodium acetate and placed in a high-pressure steel bomb. One hundred milliliters of absolute ethanol was added, followed by 3 g of 10% palladium on carbon. The bomb was closed, evacuated and purged with nitrogen, and reevacuated. The bomb was then pressurized with 1500 psi of hydrogen and maintained at this pressure for 48 hr with shaking. The bomb was vented and opened, the slurry filtered, and the alcohol extract diluted with an equal volume of water. The alcohol–water mixture was extracted with five 50-ml portions of *n*-hexane and dried ($MgSO_4$). Removal of *n*-hexane by distillation afforded 110 mg of a liquid residue. Examination of this on a 25-ft silicon

Table III. Atomic Parameters for Compound 1 (×10^4)

Atom	X	Y	Z
Cl(1)	1561 (1)	2123 (1)	1726 (2)
Cl(2)	3472 (1)	1969 (1)	5385 (2)
Cl(3)	1712 (1)	2190 (1)	6906 (2)
Cl(4)	264 (1)	3479 (1)	5633 (2)
Cl(5)	767 (1)	4604 (1)	3187 (2)
Cl(6)	1761 (1)	5395 (1)	7080 (2)
Cl(7)	3748 (1)	4792 (1)	8790 (2)
Cl(8)	4675 (1)	3510 (1)	6469 (2)
Cl(9)	3744 (1)	4942 (1)	3705 (2)
Cl(10)	4938 (1)	3497 (1)	1962 (2)
Cl(11)	3579 (1)	1760 (1)	725 (2)
Cl(12)	1957 (1)	3916 (1)	655 (2)
C(1)	2520 (3)	2792 (2)	2808 (6)
C(2)	2837 (3)	2820 (2)	4923 (6)
C(3)	1950 (3)	2869 (3)	5639 (6)
C(4)	1343 (3)	3404 (2)	5110 (6)
C(5)	1705 (3)	4073 (2)	4260 (6)
C(6)	2276 (3)	4606 (2)	5968 (6)
C(7)	3108 (3)	4351 (2)	6693 (6)
C(8)	3502 (3)	3671 (2)	5518 (6)
C(9)	3406 (3)	3932 (2)	3606 (6)
C(10)	3873 (3)	3332 (3)	2409 (6)
C(11)	3360 (3)	2659 (3)	1942 (6)
C(12)	2346 (3)	3701 (2)	2856 (6)
Cl(1')	5708 (1)	1738 (1)	4126 (2)
Cl(2')	6286 (1)	116 (1)	6510 (2)
Cl(3')	5872 (1)	1592 (1)	9152 (2)
Cl(4')	6782 (1)	3291 (1)	9189 (2)
Cl(5')	8062 (1)	3435 (1)	6556 (2)
Cl(6')	9338 (1)	2936 (1)	9914 (2)
Cl(7')	9445 (1)	1082 (1)	10183 (2)
Cl(8')	8363 (1)	−171 (1)	7025 (2)
Cl(9')	9499 (1)	1231 (1)	5165 (2)
Cl(10')	8365 (1)	−280 (1)	2305 (2)
Cl(11')	6016 (1)	−1 (1)	1797 (2)
Cl(12')	7731 (1)	2239 (1)	3116 (2)
C(1')	6773 (3)	1269 (2)	4709 (6)
C(2')	6953 (3)	999 (2)	6598 (6)
C(3')	6693 (3)	1706 (3)	7906 (6)
C(4')	7048 (3)	2425 (3)	7885 (6)
C(5')	7861 (3)	2449 (2)	6925 (6)
C(6')	8664 (3)	2205 (3)	8341 (6)
C(7')	8703 (3)	1431 (3)	8463 (6)
C(8')	8102 (3)	841 (2)	6901 (6)
C(9')	8308 (3)	1061 (2)	5113 (6)
C(10')	7811 (3)	455 (2)	3485 (6)
C(11')	6914 (3)	571 (2)	3268 (6)
C(12')	7681 (3)	1809 (2)	5033 (6)

Table IV. Anisotropic Thermal Parameters for Compound 1 (×10^4)[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	29 (1)	23 (1)	168 (3)	−6 (1)	−3 (1)	−1 (1)
Cl(2)	34 (1)	18 (1)	202 (3)	7 (1)	10 (1)	20 (1)
Cl(3)	45 (1)	30 (1)	218 (3)	−3 (1)	32 (1)	39 (1)
Cl(4)	29 (1)	36 (1)	318 (4)	6 (1)	55 (1)	32 (1)
Cl(5)	29 (1)	28 (1)	205 (3)	11 (1)	7 (1)	19 (1)
Cl(6)	44 (1)	26 (1)	203 (3)	10 (1)	25 (1)	−13 (1)
Cl(7)	42 (1)	30 (1)	120 (2)	−2 (1)	2 (1)	−7 (1)
Cl(8)	20 (1)	27 (1)	172 (3)	2 (1)	−2 (1)	9 (1)
Cl(9)	38 (1)	19 (1)	181 (3)	−5 (1)	19 (1)	14 (1)
Cl(10)	30 (1)	40 (1)	215 (3)	2 (1)	41 (1)	20 (1)
Cl(11)	44 (1)	29 (1)	183 (3)	10 (1)	18 (1)	−20 (1)
Cl(12)	39 (1)	33 (1)	126 (3)	6 (1)	4 (1)	23 (1)
C(1)	22 (2)	13 (2)	133 (10)	−1 (1)	4 (4)	−2 (3)
C(2)	28 (2)	16 (2)	130 (10)	4 (1)	14 (4)	16 (3)
C(3)	26 (2)	23 (2)	132 (10)	−6 (2)	20 (4)	8 (3)
C(4)	22 (2)	22 (2)	152 (10)	−1 (2)	18 (4)	7 (3)
C(5)	23 (2)	19 (2)	147 (10)	6 (2)	11 (4)	12 (3)
C(6)	31 (2)	17 (2)	138 (10)	4 (2)	20 (4)	6 (3)
C(7)	28 (2)	16 (2)	106 (9)	−4 (2)	6 (4)	1 (3)
C(8)	18 (2)	24 (2)	111 (9)	2 (1)	4 (3)	5 (3)
C(9)	25 (2)	16 (2)	143 (10)	−2 (1)	13 (4)	11 (3)
C(10)	21 (2)	30 (2)	141 (10)	3 (2)	15 (4)	13 (4)
C(11)	25 (2)	22 (2)	120 (9)	7 (2)	11 (4)	−2 (3)
C(12)	27 (2)	19 (2)	122 (9)	1 (2)	14 (4)	7 (3)
Cl(1')	25 (1)	33 (1)	178 (3)	10 (1)	−4 (1)	2 (1)
Cl(2')	42 (1)	23 (1)	207 (3)	−10 (1)	31 (1)	5 (1)
Cl(3')	41 (1)	42 (1)	169 (3)	−6 (1)	42 (1)	−1 (1)
Cl(4')	41 (1)	26 (1)	175 (3)	4 (1)	19 (1)	−19 (1)
Cl(5')	46 (1)	16 (1)	208 (3)	−1 (1)	20 (1)	11 (1)
Cl(6')	40 (1)	31 (1)	210 (3)	−7 (1)	−25 (1)	−8 (1)
Cl(7')	45 (1)	38 (1)	179 (3)	−1 (1)	−24 (1)	35 (1)
Cl(8')	46 (1)	19 (1)	203 (3)	6 (1)	8 (1)	24 (1)
Cl(9')	23 (1)	34 (1)	199 (3)	1 (1)	23 (1)	15 (1)
Cl(10')	54 (1)	24 (1)	205 (3)	7 (1)	49 (1)	0 (1)
Cl(11')	41 (1)	31 (1)	177 (3)	−7 (1)	−3 (1)	−19 (1)
Cl(12')	51 (1)	26 (1)	137 (3)	0 (1)	15 (1)	24 (1)
C(1')	24 (2)	19 (2)	136 (10)	4 (2)	5 (4)	8 (3)
C(2')	28 (2)	19 (2)	142 (10)	−2 (2)	19 (4)	4 (3)
C(3')	24 (2)	28 (2)	120 (10)	3 (2)	4 (4)	8 (3)
C(4')	29 (2)	23 (2)	128 (10)	3 (2)	2 (4)	3 (3)
C(5')	26 (2)	17 (2)	152 (10)	0 (2)	11 (4)	7 (3)
C(6')	20 (2)	24 (2)	153 (10)	0 (2)	8 (4)	5 (3)
C(7')	18 (2)	27 (2)	125 (10)	1 (2)	3 (4)	14 (3)
C(8')	32 (2)	16 (2)	124 (9)	3 (2)	7 (4)	14 (3)
C(9')	22 (2)	19 (2)	144 (10)	2 (1)	17 (4)	10 (3)
C(10')	36 (3)	18 (2)	128 (10)	0 (2)	13 (4)	4 (3)
C(11')	31 (2)	21 (2)	110 (10)	−3 (2)	6 (4)	6 (3)
C(12')	26 (2)	19 (2)	115 (10)	0 (2)	9 (4)	13 (3)

[a] The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

oil (SE 30) column at 190° showed seven different products, none of which had a retention time of an authentic sample of cyclododecane.

Dehalogenation of 1. A mixture of 1.0 g of **1,** 2.0 g of finely divided copper powder, and 20 ml of *n*-heptane was refluxed for 65 hr. The insoluble material was filtered and subjected to continuous extraction by *n*-hexane. The *n*-hexane solution was concentrated to afford 0.45 g of perchloroacenaphthylene, mp 375°, identified by comparison of its infrared spectrum with that of an authentic sample.[9]

In an alternate experiment, 0.57 g of **1** and 2.5 g of triethyl phosphite were dissolved in 30 ml of hexane, and the mixture was gently refluxed for 1 hr. The orange slurry was cooled and filtered to give 0.37 g (88%) of perchloroacenaphthylene.

Thermolysis of 1. A 1.0-g sample of **1** was placed in a 4-in. test tube provided with an inlet and outlet. Nitrogen was passed through the inlet and allowed to bubble through the outlet into a solution of silver nitrate. The test tube was placed in an oil bath that was preheated to 200° and maintained at this temperature for 20 min. The silver nitrate solution became cloudy and soon a precipitate of silver chloride had formed. The test tube and contents were allowed to come to room temperature. The orange-yellow oily paste that was present in the test tube was treated with 10 ml of hexane, stirred, and cooled to 0°C. After 24 hr, a white solid had crystallized, which was recrystallized from hot hexane to furnish 0.21 g (28%) of colorless needles of perchloroacenaphthene, mp 255–260° (ir spectrum was identical with that of an authentic sample).[9]

Photodecomposition of Tetrachlorodiazocyclopentadiene in the Presence of Octachlorocycloheptatriene. A solution of 1.0 g of tetrachlorodiazocyclopentadiene and 1.7 g of octachlorocycloheptatriene in 10 ml of benzene was irradiated through Pyrex glass by a high-pressure mercury lamp for 2 hr. Nitrogen evolution was brisk at the beginning but slowed down after 90 min. The dark brown benzene solution was concentrated under vacuum to furnish a brown oil. Attempted chromatography on neutral alumina using hexane as eluent resulted in decomposition of the product. The only isolable product from the eluent was a small amount of unreacted octachlorocycloheptatriene.

Collection and Reduction of the X-Ray Diffraction Data. The crystal chosen was an approximate hexagonal rod with sides centrosymmetrically bounded by the following planes (each defined by the perpendicular distance from a common origin within the crystal): ±[(120, 0.082 mm), ($1\bar{2}0$, 0.095 mm), (100, 0.097 mm)]. The top and bottom faces of the rod were likewise defined by ($11\bar{2}$, 0.140 mm) and (001, 0.15 mm), respectively. The crystal was placed on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromated Mo Kα source. The preliminary Syntex routines[15] indicated a triclinic unit cell with a = 14.655 (5) Å, b = 16.874 (5) Å, c = 7.637 (1) Å, α = 100.43 (2)°, β = 102.19 (2)°, γ = 89.89 (2)°, V = 1814.0 (8) Å^3, and with Z = 4. The calculated density of 2.09 g/cm^3 agrees within experimental error with the observed value of 2.07 g/cm^3, which was determined by flotation in a mixture of 1,3-dibromopropane and 1,2-dibromoethane.

Intensity data were collected in the range $2° \leq 2\theta \leq 45°$ using the variable-scan speed mode (2-24°/min). The intensities of two standard peaks were monitored every 50 reflections and showed a systematic decrease of 4% throughout the collection of the data. The data were reduced[16] in the usual fashion and normalized for the intensity decay to yield 4735 independent reflections of which 3663 (with $I > 2\sigma(I)$) were used throughout the structural analysis. No absorption correction was applied as the maximum range in transmission coefficients for the cylindrical crystal (μ = 18.08 cm^{-1}) was 0.73 to 0.77.

Solution and Refinement of the Structure. The solution of the structure was accomplished by direct methods and required the location of two independent molecules of $C_{12}Cl_{12}$. Statistical Wilson analysis of the data indicated a centrosymmetric distribution of intensities, later confirmed by the successful solution and refinement of the structure. The resulting 699 largest E values were processed through the multiple solution symbolic addition method of Germain, Main, and Woolfson.[17] In addition to the three origin-fixing reflections and one reflection phased from the Σ_1 formula, nine reflections were allowed as an initial basis set. Of the 2^9 (512) possibilities, the correct solution had the 13th lowest residual value and yielded the coordinates for all chlorine atoms. These chlorines were used to phase a conventional Fourier map (R_1 = 31.5)[18] which revealed the entire crystal structure.

Isotropic full-matrix least-squares[19] refinement converged at R_1 = 10.2% and R_2 = 12.9%. Block diagonalized anisotropic refinement[20] converged at R_1 = 3.2% and R_2 = 4.0%. A final full-matrix cycle varying only the x,y,z positional parameters (Table III) indicated complete convergence of the block diagonal results with the maximum shift in any coordinate of 0.12σ.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm 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 \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6785.

References and Notes

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(10) We thank Professor J. D. Roberts of California Institute of Technology for the ^{13}C spectrum of **1**.

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(15) R. A. Sparks, "Operations Manual, Syntex P$\bar{1}$ Diffractometer", Syntex Analytical Instruments, Cupertino, Calif., 1970. The conventional Delaunay reduced cell was chosen directly from the Syntex output. The triclinic Laue symmetry and associated lattice lengths were verified by partial rotation photographs along each of the three reciprocal axes. In addition, there is no evidence for a higher lattice symmetry, either from the lattice scalars corresponding to this reduced cell, from an examination of the full matrix correlation terms of the final least-squares, or from a careful examination of the crystal packing.

(16) The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_R]\,T_R$, where S is the scan counts, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time (B_R = 0.67 for this data set), and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R\,[S + (B_1 + B_2)/B_R{}^2 + q(I)^2]^{1/2}$, where q in this case was set equal to 0.003. All crystallographic programs used in structural determination and least-squares refinement were written by one of us (J.C.C.). The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

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(19) All least-squares refinement were based on the minimization of $\Sigma w_i\|F_o| - |F_c\|^2$ with the individual weights $w_1 = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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