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X-ray Analysis, Molecular Structure, and Nuclear Magnetic Resonance Spectra of a Dimer from 1,1-Dichloro-2,5-diphenylcyclopropabenzene: (*E*)-2,2′,3,3′-Tetrachloro-4,4′,7,7′-tetraphenyl-1,1′-bicycloheptatrienylidene

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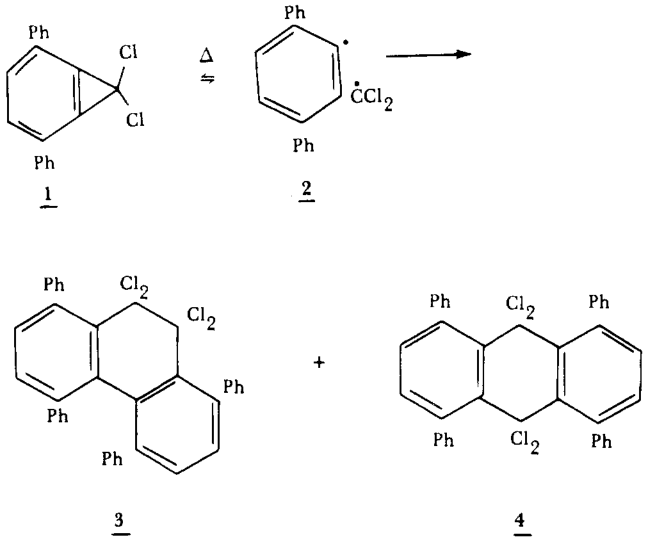
The molecular structure of one of two dimers, $C_{38}H_{24}Cl_4$, produced by thermal reaction of 1,1-dichloro-2,5-diphenylcyclopropabenzene (1) has been revealed by crystallographic analysis to be a novel heptafulvalene, (*E*)-2,2′,3,3′-tetrachloro-4,4′,7,7′-tetraphenyl-1,1′-bicycloheptatrienylidene (10) in which the two seven-numbered rings are bent up facing each other. Previously reported spectroscopic data and new higher resolution NMR data can now be rationalized.

The past decade has seen significant advances in cyclopropabenzene chemistry.[1] For example, the reactivity associated with 1,1-dichloro-2,5-diphenylcyclopropabenzene (1)[2] has been utilized in the production of the hydrocarbon,[3] the 1,1-difluoro-,[4] 1,1-dialkyl-,[5] and 1,1-diaryl-,[5] derivatives, and also the corresponding cyclopropabenzenyl cation.[6] Despite the ease with which these reactions can be performed, the chemistry of 1 has been complicated by its ready decomposition under a variety of conditions. We have reported previously on the rapid formation of ortho esters and carboxylate esters from 1 in alcoholic media[2] and on the formation of tropones and dimers induced by acid and by heat.[7] Thermal decomposition of 1 in benzene or acetone solution affords two crystalline dimers, $C_{38}H_{24}Cl_4$.[7] The spectroscopic data for both the pale yellow dimer A and the bright yellow dimer B were apparently inconsistent in one aspect or another with those expected for all the most likely compounds.

Scheme I



Thermolysis of 1 might be expected to result in the sterically crowded dihydroaromatics 3 and 4 by head-to-head and head-to-tail coupling of the diradical 2 (Scheme I), by analogy with the formation of 9,10-dihydrophenanthrene from parent cyclopropabenzene.[8] However, the ^{1}H FT NMR spectra of A and B eliminated the symmetrical dihydroanthracene 4 from consideration since *both* dimers exhibited an AM pattern for four of the aromatic protons.[7] Furthermore, the ^{13}C FT NMR spectra of the two dimers were very similar and did not show a carbon resonance for a CCl_2 moiety in the region where those of independently synthesized 1,1,2,2-tetrachloro-1,2-diphenylethane[9] appear (δ 99.3).[10] These observations, coupled with the failure to effect either nucleophilic substitution or carbonyl generation with silver trifluoroacetate[11] with each dimer, eliminated compounds 3 and 4 as possible structures for the dimers.

If thermolysis occurred by a 1,2-chloride shift to give intermediate 5 followed by rearrangement, then a further three sets of dimers are possible (Scheme II). The stilbenes 6 were excluded since the ^{1}H spectra showed relatively shielded AM patterns (δ 6.23, 6.83) inconsistent with published data for stilbenes.[12] Dimerization of the cyclic

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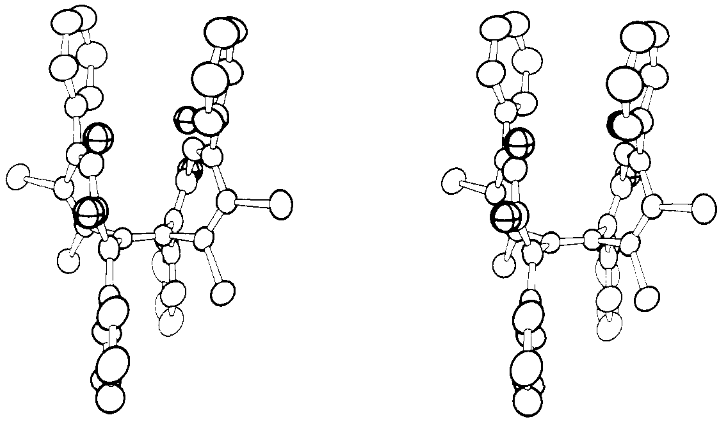

Figure 1. Stereoscopic diagram of the molecular structure. The four hydrogen atoms on the seven-membered rings are represented by darkened spheres with the equator and three meridians drawn in. This diagram was computer produced.[25]

Scheme II

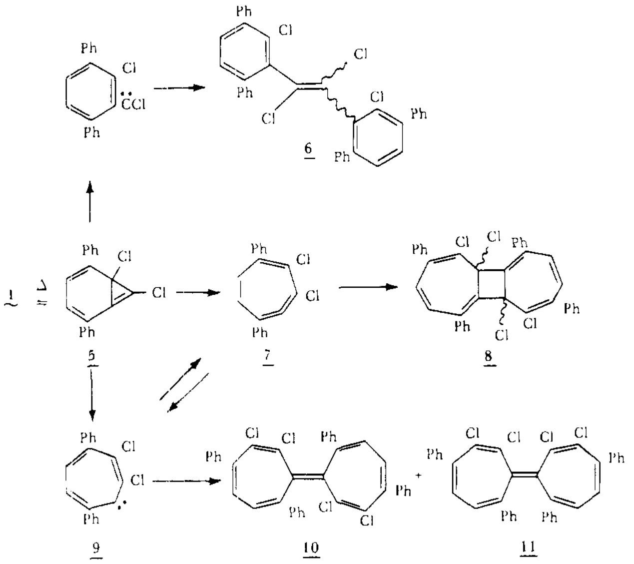

Table I. Crystal Data

formula	$C_{38}H_{24}Cl_4$	*a*	7.852 (1)[a] Å
mol wt	622.427	*b*	11.402 (2) Å
space group	*P*2/*c*	*c*	17.744 (3) Å
ρ_x (2 $C_{38}H_{24}Cl_4$/cell)	1.344 g cm^{-3}	β	104.57 (1)°
ρ_m (CCl_4/hexane, 27 °C)	1.343 g cm^{-3}		

[a] Here and subsequently the standard deviation is given in multiples of the least significant figure quoted.

allene 7 would yield isomeric tricyclo[7.5.0.0^{2,8}]tetradecahexaenes 8,[13] but the ^{13}C spectra failed to exhibit any chlorine-bearing tetrahedral carbons, even after the addition of tris(acetylacetonato)chromium(III)[14] to the solution. Dimerization of the carbene 9, for which there is ample evidence,[15] would afford the bicycloheptatrienylidenes (heptafulvalenes) 10 and 11. Similar, but less substituted, compounds are intensely colored (red to black) and undergo fragmentation on electron impact in a different manner than that for 10 and 11.[15] For example, 2,2′-diphenylbicycloheptatrienylidene gives a base peak of *m*/*e* 178 ($M^{+\cdot} - 2C_6H_5$).[15b] The relatively pale color of the dimers A and B and the observation of base peaks at *m*/*e* 552 ($M^+ - Cl_2$) were thus apparently inconsistent with structures 10 and 11.

We now wish to report the X-ray crystallographic analysis of one of these dimers, "pale yellow dimer A",[7] which shows that it is indeed a heptafulvalene, (*E*)-2,2′,3,3′-tetrachloro-4,4′,7,7′-tetraphenyl-1,1′-bicycloheptatrienylidene (10), in a novel conformation in which the two seven-membered rings are bent up facing one another. Rationalization of the spectroscopic data, including new ^1H and ^{13}C NMR data obtained at 23.5 and 63 kG, is now possible.

X-ray Analysis

Experimental Methods. Both dimers were recrystallized from acetone, and a specimen (0.20 × 0.28 × 0.28 mm) of the pale yellow dimer A was chosen for study. The possible space groups *Pc* and *P*2/*c* were deduced from the diffraction symmetry and the systematic absences. Unit cell parameters and intensity data were obtained by using Cu Kα radiation (graphite monochromated, λ = 1.540 51 Å) on a CAD4 diffractometer. Data reduction yielded 3113 unique reflections, corrected for absorption and polarization, from the two quadrants collected. Table I contains some crystallographic quantities. Application of the MULTAN system of programs[16] revealed a plausible model which surrounded a diad in space group *P*2/*c*. Conventional difference Fourier and least-squares methods were used to complete and refine the model. Final least-squares refinement cycles were performed with 238 variables against the 2969 data with $F^2 > 0$ by using standard scattering factors.[17-19] Shifts in the last cycle were $\leq 0.50\sigma$. The unweighted and weighted *R* values at convergence were 0.055 and 0.050, respectively. Tabulations of the final positional and thermal parameters and a listing of the observed and calculated structure factors are available as supplementary material.

Discussion. As indicated above the crystallographic asymmetric unit comprises only half of the molecule. The second half (atoms designated by primes) is identical with the first by virtue of a twofold axis of symmetry. The parallel arrangement of the two seven-membered rings, shown stereoscopically in Figure 1, allows the bulky substituent groups to project from the periphery of the molecule, thus avoiding any unusual intramolecular con-

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Table II. Endocyclic Torsion Angles (in Degrees)

C(7)–C(1)–C(2)–C(3)	+66.6
C(1)–C(2)=C(3)–C(4)	+4.7
C(2)–C(3)–C(4)–C(5)	−42.4
C(3)–C(4)=C(5)–C(6)	+0.9
C(4)–C(5)–C(6)–C(7)	+36.9
C(5)–C(6)=C(7)–C(1)	+3.9
C(6)–C(7)–C(1)–C(2)	−70.2

tacts. The resulting puckered conformation of the nonaromatic rings also prevents cross conjugation between the two rings which explains the lack of intense color and the dissimilarity of its ultraviolet spectrum with those reported for less substituted heptafulvalenes.[15]

Figure 2 shows bond lengths (uncorrected for thermal motion) and bond angles in the two seven-membered rings. The average endocyclic ring angle of 120.7° is less than the 126.7° value found in the less sterically hindered parent heptafulvalene structure.[20] Steric repulsions between bulky substituents cause appreciable distortions from the planar conformation, and as a result the ring angles may assume values closer to the ideal sp^2 angle of 120°. This deformation, expressed in terms of the torsion angles listed in Table II, shows only small rotations about the double bonds and large rotations about the single bonds. Since the overlap between π orbitals, and therefore the amount of conjugation, is decreased with increasing torsion, the double bonds tend to be isolated from one another by the large twists around the single bonds as is evident in Figure 2 by the alternation of double and single bond lengths. Steric interactions are also exhibited in the difference between the torsion angle of −37.7° between the plane formed by C(3)–C(4)–C(5) and the more hindered phenyl ring and the 24.9° angle between the plane formed by C(1)–C(7)–C(6) and the more isolated phenyl ring. The latter value compares well with the 23° angle between the tropylium and phenyl rings found by Takusagawa and Jacobson in phenyltropylium fluoroborate–triphenylmethyl fluoride.[21] The former value appears to be the result of intramolecular interactions between the two parallel phenyl rings on C(4) and C(4′). Although the bond distances and angles between the phenyl carbon atoms show some variation, the average values in each group are quite reasonable. The average values are as follows: C–C 1.384 Å and C–C–C 120.0°. C–H bond lengths are in the usual range. No unusual intramolecular H···H contacts were evident.

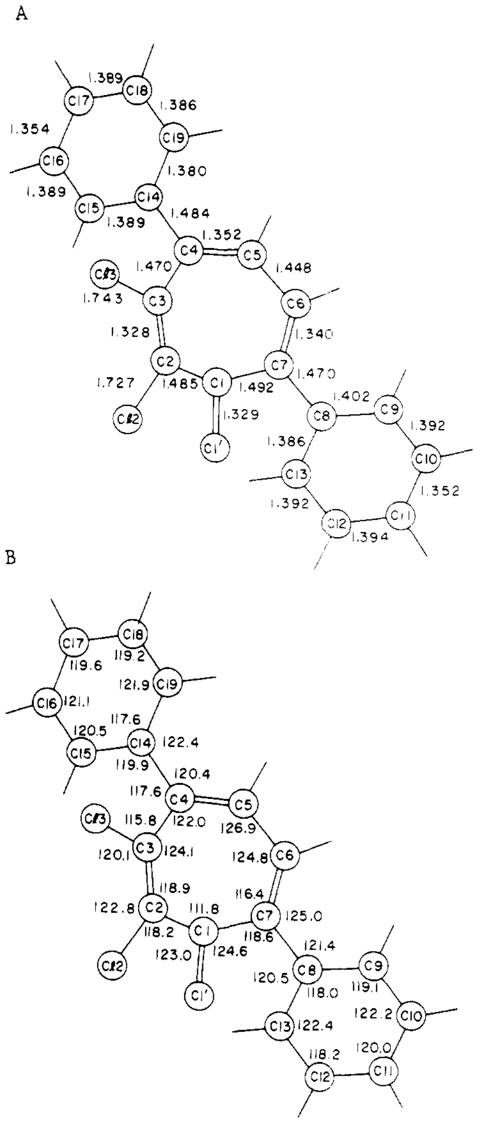

Figure 2. Bond distances (part A) and interbond angles (part B) for the crystallographically unique half of compound **10**. Atom Cl′ is symmetry related to atom Cl by a twofold axis which is orthogonal to the Cl–Cl′ bond through its midpoint. Standard deviations for the average 0.003 Å for the C–Cl bonds and 0.004 Å for the C–C bonds. The C–C–Cl angles have a standard deviation of 0.1° and the mean σ for the C–C–C angles is 0.2°.

NMR Spectra

Experimental Methods. The spectra were recorded on a JEOL FX-100 instrument operating at 99.54 MHz for ^1H and 25.00 MHz for ^{13}C. The ^1H spectra were obtained for a 0.016 M solution in CD_2Cl_2 by using 16K data points, a 1000-Hz spectral width, and a pulse angle of 45° (5 μs) (digital resolution 0.12 Hz). Ten transients were accumulated and exponentially broadened by 0.02 Hz. Chemical shifts are reported in parts per million from internal Me_4Si and are the centroids of each multiplet. They are not values from iterative spin analysis.

The ^{13}C spectra were obtained for a 0.09 M solution in CD_2Cl_2 by using 16K data points, a 4000-Hz spectral width, and a pulse angle of 45° (11 μs). Typically, 600 transients were accumulated for the proton noise decoupled spectra and 1000 transients for off-resonance and selective decoupled spectra. Exponential broadening of 0.25 Hz was applied prior to transformation. Chemical shifts are reported ±0.02 ppm from internal Me_4Si. The 67.89-MHz ^{13}C spectrum was recorded on the same solution on a Bruker HX-270 spectrometer with 32K data points and a spectral width of 15000 Hz. The 270-MHz (63 kG) proton spectrum was recorded on the same instrument.

Discussion. At 100 MHz the ^1H NMR spectrum of **10** in CD_2Cl_2 shows an AM pattern[22] at δ 6.23 (J = 6.1 Hz) and 6.83. Inspection of a model of the structure shown in Figure 1 shows that H(5) lies above the plane of the phenyl ring attached to C(4′) on the other half of the molecule whereas H(6) lies in the plane of the phenyl substituent on C(7). Thus the low-frequency resonance at δ 6.23 can be assigned to H(5) [H(5′)] and thereby that at δ 6.83 to H(6) [H(6′)]. Both resonances are relatively deshielded compared to less substituted heptafulvalenes.[15b]

The phenyl proton resonances, which appeared as three multiplets at 60 MHz, comprise four multiplets in the

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[22] The pattern is almost of the AX type with the outer transitions only slightly weaker than the inner ones.

Table III. NMR Spectral Data[a] of **10** Determined in CD_2Cl_2

position	$^1H^b$	$^{13}C^{c,d}$
1		137.35 (s)
2		139.36 (s)
3		119.09 (s)
4		139.27 (s)
5	6.23 (1 H, d, J = 6.1 Hz)	129.78 (d)
6	6.83 (1 H, d, J = 6.1 Hz)	121.29 (d)
7		139.27 (s)
8		139.54 (s)
9, 13	7.87 (2 H, dd)[f]	127.53 (d)
10, 12	7.50 (3 H, m)[g]	129.05 (d)
11		129.01[e] (d)
14		140.21 (s)
15, 19	7.00 (2 H, dd)	127.49 (d)
16, 18	7.21 (3 H, m)[g]	128.27 (d)
17		128.06 (d)

[a] In parts per million relative to Me_4Si. [b] Chemical shifts are given as the centroid of the multiplets. [c] ±0.02 ppm. [d] Assignments of all quaternary carbons are uncertain. [e] Resolved at 63 kG. [f] Approximately doublet of doublets. [g] Second order at 63 kG.

order δ 7.00 (2 H), 7.21 (3 H), 7.50 (3 H), and 7.87 (2 H) (for half the molecule, Table III). Double-irradiation experiments show that the two low-frequency multiplets at δ 7.00 and 7.21 are part of one phenyl ring and the other two multiplets part of the other phenyl ring. Furthermore, the splitting patterns (approximately doublet of doublets) of the multiplets at δ 7.00 and 7.87 allow these multiplets to be assigned to ortho protons. Since the structure of **10** shows H(15) and H(19) after rotation about C(4)–C(14) also to be in the shielding zone of the C(7′) phenyl group, the resonance at low frequency (δ 7.00) can be assigned to H(15) [H(19)], that at δ 7.21 to H(16), H(17), and H(18), that at δ 7.50 to H(10), H(11), and H(12), and that at δ 7.87 to H(9) and H(13). At 270 MHz the proton spectrum still showed second-order characteristics for all the absorptions [except for H(5) and H(6)], and coupling constants were not determined (Table III).

The assignment of the ^{13}C resonances of the protonated carbons is made on the basis of the above proton assignments and selective decoupling experiments. Thus the proton at δ 6.23 is attached to the carbon which resonates at δ 129.78 while the proton at δ 6.83 is attached to the carbon which resonates at δ 121.29. This is a striking example of the fact that anisotropy of phenyl rings is a major factor in ^1H shielding but is relatively minor in ^{13}C shielding.[23] The meta carbons in both phenyl rings are equivalent, but two separate ortho resonances are just discernible at 25 MHz. This separation is well resolved (0.06 ppm) at 68 MHz, and, in addition, a separate one-carbon (protonated) resonance is observed 0.04 ppm to lower frequency than that at δ 129.05 [C(10), C(12)]. This is assigned to C(11).

Assignment of the resonances due to quaternary carbons is much less certain. Of the expected seven lines only six are observed at 25 MHz and only five at 68 MHz. The two very low intensity lines at δ 139.36 and 119.09 have been assigned to the chlorinated carbons C(2) and C(3) since these would be expected to have the longest relaxation times. At 68 MHz and with the same spectrometer recycle time, the intensity of the line at δ 119.09 is exceptionally low, indicating a significant contribution from chemical shift anisotropy to the relaxation of the carbon nucleus. The relative order of the assignments is based on the previous assignment in heptafulvalenes, the carbon closest to the exocyclic bond being at highest frequency.[24] Also C(3) is expected to experience a low-frequency, "γ-effect" shift because of its position between two bulky groups. The other quaternary carbon resonances cannot be assigned with any certainty at this stage.

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Registry No. 1, 33253-76-8; 10, 65961-16-2.

Supplementary Material Available: Tables of atomic coordinates and thermal vibration parameters for all atoms and bond distances for the hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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