7,8-(Dichloromethano)homo[70]fullerene, an Unusual, but Unexceptional, Methanoannulene

by **Andrew F. Kiely**, **Mark S. Meier**, **Brian O. Patrick**, **John P. Selegue**, and **Carolyn Pratt Brock***

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

For *Jack Dunitz*

The crystal structure of 7,8-(dichloromethano)homo[70]fullerene shows that addition of the dichlorocarbene (:CCl_2) to C_{70} gives a surprisingly normal methano-bridged [9]annulene. The structural changes caused by the addition are highly localized; the C(7)–C(8) distance lengthens by 0.705(2) Å but no other distance changes by more than 0.022(3) Å. Bond angles within the [9]annulene increase by as much as 7.8(1)°, but changes outside the C_9 ring are much smaller. The nearly ellipsoidal molecules form hexagonally close-packed layers that interact in pairs through short Cl···C, and possibly short Cl···Cl and C···C, interactions.

Introduction. – What happens to the bond lengths and angles in a fullerene when one of its bonds is broken? If the reaction is the addition of a carbene, how is the resulting bridged annulene affected by being embedded in a fullerene cage?

Early reviews by *Wudl* [1] and a later review of methanofullerenes by *Diederich et al.* [2] indicate that carbene additions to fullerenes produce only two of the four possible kinds of isomers. Of the two types of observed isomers, the [6,6]-closed methanofullerenes are the more stable and the [6,5]-open methanofullerenes ('fullerenoids') the less stable. The [6,5]-closed methanofullerenes, a third kind of isomer, are inferred as intermediates in rearrangements of [6,5]-open to [6,6]-closed methanofullerenes. The [6,6]-open fullerenes, the fourth isomer type, are calculated to be very unstable. Reactions of dichlorocarbene (:CCl_2) with C_{60} are reported to give only the [6,6]-open isomer $C_{61}Cl_2$ [3], but addition of a :CCl_2 to C_{70} gives several products, one of which is a [6,5]-open isomer $C_{71}Cl_2$ [4].

A preliminary report of the structure of a [6,5]-open isomer, *i.e.*, 7,8-(dichloromethano)homo[70]fullerene, has already appeared [4]. We believe (*cf.* [5]) that no other reliable structure of an open fullerene with one broken bond has yet been published. The structure of [bis(4,4′-bromophenyl)methano]homo[60]fullerene has been reported [6], but the crystals were small, twinned, and compositionally disordered. The occupancy factor was 0.34 for the [6,5]-open isomer but 0.66 for the [6,6]-closed isomer. The length determined for the nonbond (1.87(14) Å) in that structure is nearly 0.3 Å shorter than was found in 7,8-(dichloromethano)homo[70]fullerene (2.14(1) Å) [4]. A distance of 1.87 Å between two C-atoms in a [10]annulene seems more likely to be bonding than nonbonding [7]. One other fullerenoid structure is known: *Rubin* and coworkers have reported the structure of the Co complex of a C_{60} derivative with a large trimethano[15]annulene opening [8]. In that structure, three bonds of the C_{60} cage are broken.

While the identity of the [6,5]-open isomer of 7,8-(dichloromethano)homo[70]fullerene reported here1)) was known previously, no analysis of the effects of the carbene addition on the rest of the molecule nor any comparison with simpler annulenes has been made.

Results of Structure Determination. – Crystal data are given in *Table 1*; the atom-numbering scheme and the definitions of the averaged bond lengths and angles are shown in *Fig. 1*. The numbering system follows the *IUPAC* guidelines issued in 1997 [9]

Table 1. *Crystallographic Data*

T [K]	110(2)	173(1)	295(1)
Formula	$C_{71}Cl_2 \cdot 0.445\ C_5H_{12} \cdot 0.055\ C_7H_8$	$C_{71}Cl_2 \cdot 0.445\ C_5H_{12} \cdot 0.055\ C_7H_8$	$C_{71}Cl_2 \cdot 0.445\ C_5H_{12} \cdot 0.055\ C_7H_8$
Formula weight [g mol^{-1}]	960.86	960.86	960.86
Crystal color	black	black	black
Crystal dimensions [mm]	0.30 × 0.18 × 0.12	0.30 × 0.18 × 0.12	0.30 × 0.18 × 0.12
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	17.876(2)	17.881(2)	17.905(3)
b [Å]	10.730(1)	10.750(1)	10.790(1)
c [Å]	37.935(4)	37.981(4)	38.106(4)
β [°]	96.75(2)	96.76(2)	96.84(2)
V [Å^3]	7225.9(13)	7250.0(13)	7309.5(16)
Z; Z'	8; 2	8; 2	8; 2
D_x [g cm^{-3}]	1.767	1.761	1.761
θ Range [°]	1.7 – 25.0	1.7 – 25.0	1.7 – 20.7
μ [mm^{-1}]	0.24	0.24	0.24
Refl. measured	177011	133891	140432
Independent refl.	12658	12710	7527
Refl. observed [$I > 2\sigma(I)$]	8032	7789	5782
Refl. used	12647	12702	7527
No. of variables	1369	1369	1369
No. of restraints	7	7	7
Final R [$F^2 > 2\sigma(F^2)$]	0.089	0.085	0.088
Final wR_2 (all refl.)	0.144	0.150	0.141
Goodness-of-fit	1.10	1.09	1.26
Weighting scheme [$P = (F_0^2 + 2F_c^2)/3$]	$w = 1/[\sigma^2(F_0^2) + (0.034P)^2 + 10.5P]$	$w = 1/[\sigma^2(F_0^2) + (0.045P)^2 + 6.7P]$	$w = 1/[\sigma^2(F_0^2) + (0.020P)^2 + 17.5P]$
Secondary extinction coefficient	$7.2(13) \times 10^{-4}$	$8.1(17) \times 10^{-4}$	$3.4(8) \times 10^{-4}$
Final $(\Delta/\sigma)_{max}$	0.00	0.01	0.01
$\Delta\rho$ (max; min) [e Å^{-3}]	+0.50, −0.42	+0.53, −0.47	+0.37, 0.30

---

1) Crystallographic data (excluding structure factors) for the structure at 110 K are available in the *Cambridge Structural Database* under the refcode CELQUF. Data for the structures at 173 and 295 K have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications No. CCDC-202910 and -202911. Copies of the latter two sets of data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223-336033; e-mail: deposit@ccdc.

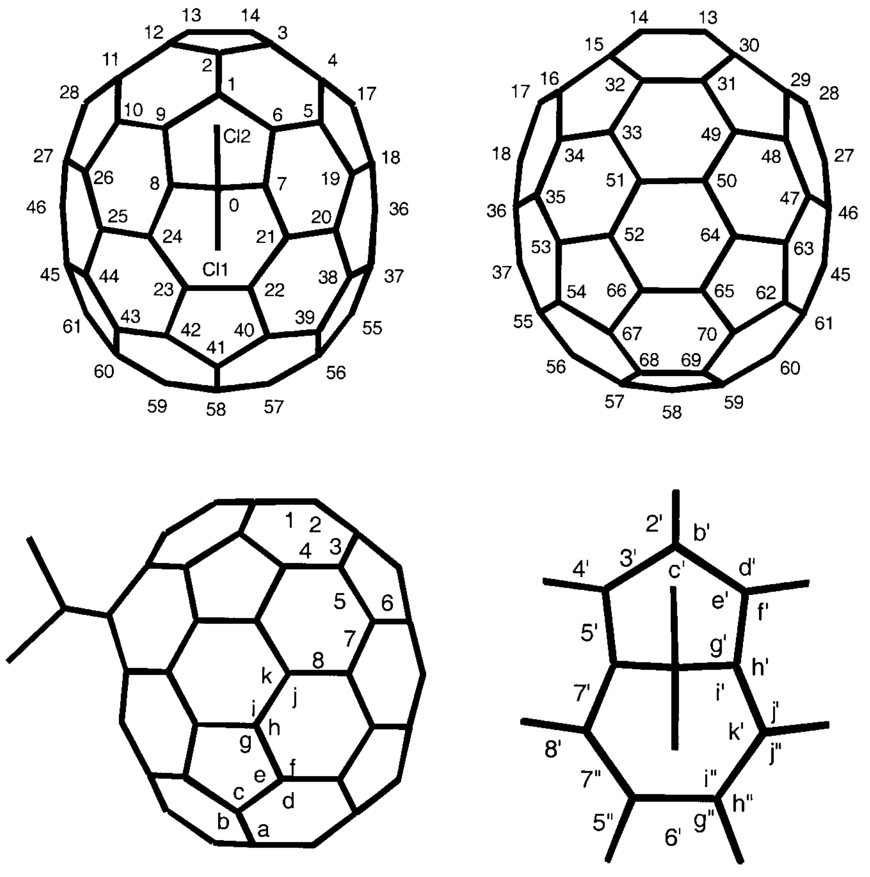

Fig. 1. *The atom-numbering scheme and the definitions used for the averages of bond lengths* (1–9 and 1′–9′) *and angles* (a–k and b′–g″). Atoms in molecule 2 are distinguished by primes (*e.g.*, C(7) and C(7′)).

rather than the revised guidelines issued in 2002 [10]; atoms in the second independent molecule are distinguished by primes. The designations of the average distances and angles follow the scheme of *Diederich* and co-workers [11]. Projections of the two independent molecules as observed at 110, 173, and 295 K are shown in *Fig. 2*. The atomic ellipsoids, which increase with temperature approximately as expected [12], suggest that most of the molecular motion is tangential.

Because there are two independent $C_{71}Cl_2$ molecules in the asymmetric unit, and because each molecule has approximate mirror symmetry, four values were determined for 49 of the 60 chemically different bond lengths. The agreement between the four (or in some cases two) chemically equivalent distances at the two lower temperatures (average e.s.d. 0.005 and 0.006 Å calculated from the spread of the values about their mean) is at least as good as could be expected given the uncertainties for the individual bond lengths (averages 0.006 Å at 110 and 173 K; ranges 0.005–0.007 Å). The uncertainties of the mean values themselves are lower by factors of $4^{1/2}$ or $2^{1/2}$.

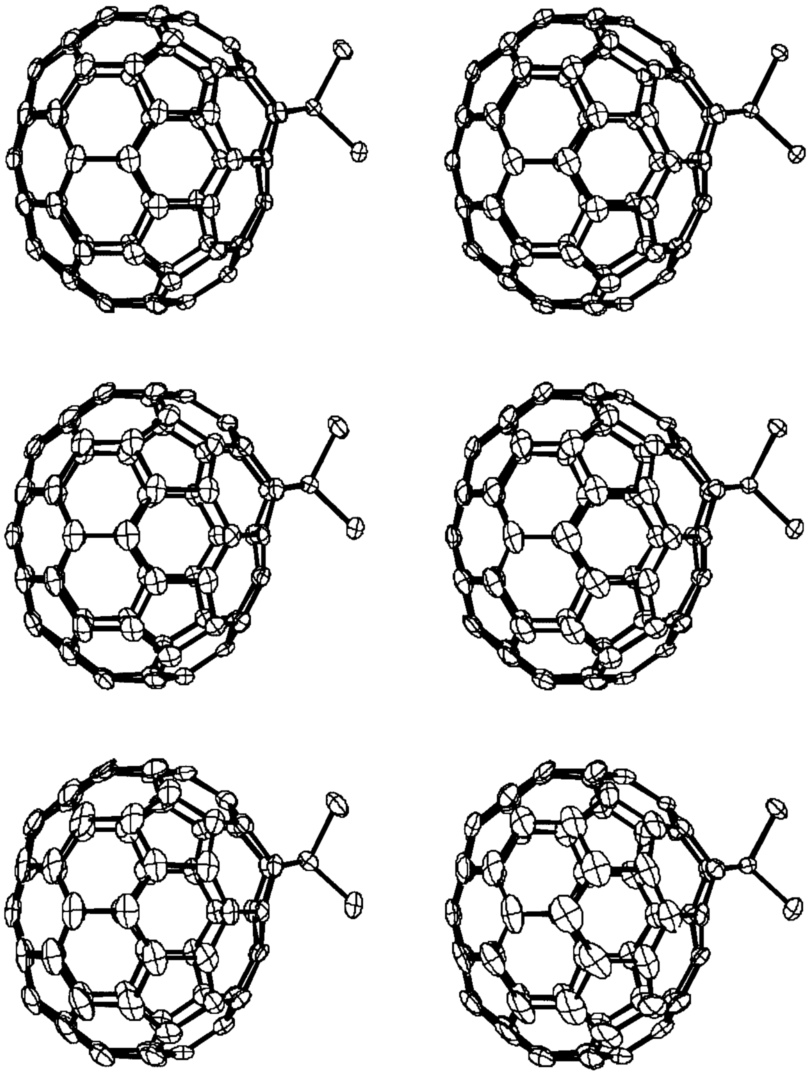

Fig. 2. *Perspective drawing of the two independent molecules of $C_{71}Cl_2$* (molecule 1 on the left) *as determined at 110 K* (top), *173 K* (middle), *and 295 K* (bottom). The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement.

Uncertainties for averages taken over bonds expected to be similar (see below) are even lower.

A simple thermal-motion analysis with PLATON [13] shows that corrections to the bond lengths for librational motion at 110 and 173 K are small and uniform. The values given here are uncorrected; corrected values would be longer by 0.002–0.003 Å. We believe the bond lengths and angles determined at the two lower temperatures to be equally reliable; the thermal motion at 110 K was lower than at 173 K, but loss during data collection at the lower temperature of a large fragment of the crystal meant the reflection intensities of many reflections were also lower. Averaging bond lengths over values determined at those two temperatures is just as successful as averaging over values for one temperature. The average difference between values averaged at 110 and at 173 K is 0.001 Å. We, therefore, report the two-temperature averages; their uncertainties are ≤ 0.003 Å and 0.01°. Bond lengths determined at 295 K are less good because of the low $\theta_{\max}$ and the greater thermal motion.

Consequences of the Carbene Addition. – Upon addition of the $:CCl_2$ the C(7)–C(8) bond is broken, and its distance changes from *ca.* 1.43 to 2.138(1) Å. The C(7)- and C(8)-atoms move out from the C_{70} shell and somewhat farther apart (see *Fig. 3*).

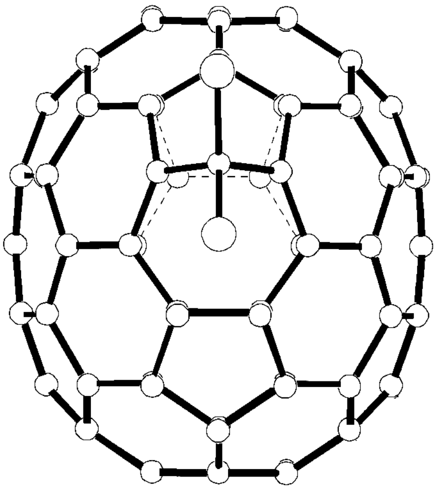

Fig. 3. *Projection of molecule 1 as determined at 110 K superimposed on the same molecule rotated by 2π/5 and taken through the mirror plane located at the molecular equator.*

The breaking of the C(7)–C(8) bond changes the positions of those atoms by nearly 0.5 Å but has only minor consequences for the rest of the molecule. Least-squares fits of the molecules with each other and with themselves were made with routine OFIT in SHELXTL PC [14]. Fits of the molecules 1 and 2 at 110 K less their CCl_2 groups (70 atoms per molecule in the fits) to the molecule rotated by $2\pi/5$ and flipped top to bottom gave r.m.s. atomic deviations of 0.125–0.127 Å. These values were reduced to 0.054 Å if C(7) and C(8) were left out of the fit, and to 0.036–0.037 Å if all atoms of the [9]annulene (C(1), C(6)–C(9), C(21)–C(24)) were also omitted. While these last r.m.s. values are low, the deviations for fits of the two molecules to each other at 110 and 173 K, and to the molecules at the other temperature are even lower (0.009–0.014 Å). There may be very subtle changes elsewhere in the molecule when the C(7)–C(8) bond is broken. If crystal-packing effects were responsible for the differences then the two independent molecules, which are not related by any obvious pseudosymmetry, would be expected to be more different.

The fits with all 70 fullerene atoms show that the displacements of C(7) and C(8) deviate from the positions expected for C_{70} by 0.47(1) Å. The deviations for the rest of the atoms in the [9]annulene are substantially smaller (0.12 Å for C(21) and C(24); 0.06 Å for C(22) and C(23); 0.06 Å for C(6) and C(9); and 0.08 for C(1); all e.s.d.s. < 0.01 Å).

Because the changes caused by carbene addition to the C_{70} cage are so localized it is possible to successfully average distances and angles over the C_{5h} symmetry of the parent molecule if the bonds and angles shown in the diagram at the bottom right of *Fig. 1*, *i.e.*, the bonds involving atoms in the [9]annulene and angles for which the central atom is part of that ring, are not included. The uncertainties for these mean values are ≤ 0.003 Å and 0.1° (see *Table 2*), *i.e.*, no larger than the uncertainties for averaging over distances and angles that are more strictly chemically equivalent. Definitions of the average bond lengths and angles are shown in *Fig. 1*; they are the same as have been used previously [11].

Table 2. *Average Bond Lengths* [Å] *and Angles* [°] *Found for* $C_{71}Cl_2$ *at 110 and 173 K and for Four Literature Structures* (CSD refcodes LAZMEE, REFTOL, ZADQUQ, and ZADRAX)[a])

Bond type	Average distance in $C_{71}Cl_2$	Average distance in literature structures	Angle type	Average angle in $C_{71}Cl_2$	Average angle in literature structures
1	1.447(2)	1.448(2)	a	119.9(1)	119.8(1)
2	1.388(2)	1.390(1)	b	120.2(1)	120.1(1)
3	1.444(1)	1.446(2)	c	107.1(1)	107.1(1)
4	1.380(1)	1.378(3)	d	120.2(1)	120.1(1)
5	1.444(1)	1.448(1)	e	108.5(1)	108.3(1)
6	1.433(2)	1.426(2)	f	120.0(1)	119.9(1)
7	1.414(1)	1.417(2)	g	108.0(1)	108.1(1)
8	1.469(3)	1.481(4)	h	121.4(1)	121.3(1)
			i	121.2(1)	121.4(1)
			j	118.7(1)	118.7(1)
			k	116.4(1)	116.0(1)

[a]) The codes for the bond lengths and angles are shown in *Fig. 1*. Numbers in parentheses are the estimated standard deviations in the least-significant digits as determined by the averaging. Bond-length averages for $C_{71}Cl_2$ do not include lengths of bonds that include one of the atoms of the [9]annulene. Bond angle averages for $C_{71}Cl_2$ do not include angles in which the central atom is part of the [9]annulene.

Comparison with Other Fullerenes. – The bond lengths and angles in the unsubstituted part of the $C_{71}Cl_2$ molecule (see *Table 2*) are in excellent agreement with those for the most precise crystal structures and for those derived from quantum-mechanical calculations. A search of version 5.24 (November 2002) of the *Cambridge Structural Database* (hereafter, the CSD) [15] turned up 38 C_{70} structures, 22 of which were published during or after 1998, the year of a major review [16]. Only one very precise (uncertainties on C−C bond lengths in the range 0.001 – 0.005 Å) C_{70} structure [17] has been reported since careful comparisons were made [11] of precise bond lengths determined for three molecules (CSD refcodes LAZMEE [18], ZADQUQ [11], and ZADRAX [11]) and of bond lengths calculated with quantum mechanics. The average bond lengths found for those three molecules change by at most 0.002 Å when the values from this study and from CSD entry REFTOL [17] are included (see *Table 2*). Note that structures LAZMEE, ZADQUQ, ZADRAX, and REFTOL were determined at 100, 193, 100, and 170 K, respectively, so that the average temperature of the $C_{71}Cl_2$ determination is similar to the average temperature for the comparison structures. This agreement provides further proof that the effects on bond lengths and angles of breaking the C(7)–C(8) bond are highly localized.

Bond Lengths and Angles in the [9]Annulene. – Details of the differences between the bond lengths and angles of the [9]annulene and those of the rest of the molecule are shown in *Fig. 4*. All five types of bonds within the [9]annulene are longer, or at least no shorter, than their comparison bonds. The changes in the bond angles are larger and reflect the distribution of the strain caused by the lengthening (0.705 (2) Å) of the C(7)–C(8) distance.

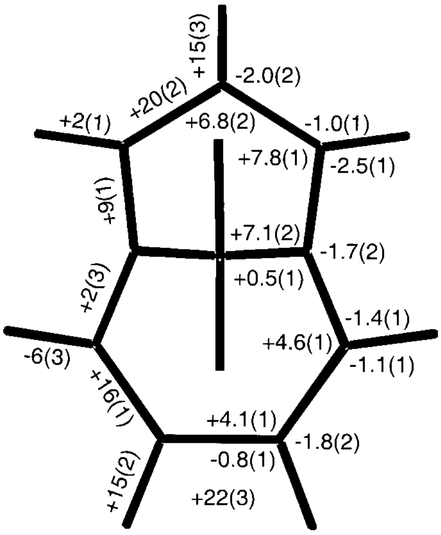

Fig. 4. *Differences between the average bond lengths* ([Å] × 10^3) *and bond angles* [°] *within and adjoining the* CCl_2*-bridged [9]annulene and the average values for the corresponding bonds in the rest of the molecule.* Bond-length differerences are shown on the left of the diagram; angle differences are shown on the right. Note that no bond length in the [9]annulene is shorter than the comparison bond. See *Fig. 1* for the labels of the bond types, and *Table 2* for the distances and angles for the unsubstituted part of the molecule. Estimated standard deviations derived from the averaging and subtraction are shown in parentheses.

The radial p orbital on C(7) is less well aligned with the radial p orbitals on C(1) and C(22) (similarly for the radial orbitals on C(8), C(1), and C(23)) after the carbene is added (average torsion angles 36.0(3)° and 27.1(1)°); on the other hand, the radial p orbitals on C(7) (and C(8)) are better aligned with those across the ring on C(5) and C(20) (and on C(10) and C(25)) (average torsion angles 173.4(1)° and 176.5(2)°). There is no major loss of π overlap upon carbene addition for the C_{70} unit as a whole, although there are significant changes in overlap for individual pairs of atoms. The ring bond lengths involving the bridgehead atom change little when the carbene is added.

Comparison with Other Annulenes. – Searches of the CSD yielded hits for 25 well-determined ($R < 0.08$) 1,6-CR_2-bridged [10]annulenes and for seven 1,5-CR_2-bridged [8]annulenes; no such [9]annulene was found. The numbers of independent molecules in these two sets of structures are 34 and 8. Plots against the nonbond length (C(7)$\cdots$C(8) for the $C_{71}Cl_2$ structure) of the bridging angle (C(7)–C(0)–C(8) for $C_{71}Cl_2$ structure) and of the average angle at the bridgehead (*e.g.*, C(6)–C(7)–C(0) in this structure) show (see *Fig. 5*) that the points for $C_{71}Cl_2$ lie on well-defined curves. In $C_{71}Cl_2$, the rest of the fullerene cage constrains the bridged annulene so that the nonbond distance is shorter than usual and the bridging angle smaller, but the [9]annulene is otherwise comparable to literature precedents.

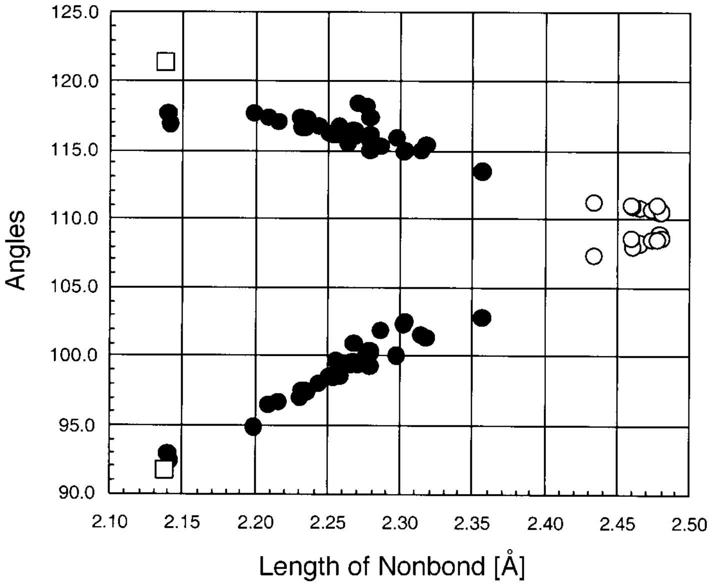

Fig. 5. *Plot of the bridging angle* (C(7)–C(0)–C(8) for $C_{71}Cl_2$) *and of the average bridgehead angle* (*e.g.*, C(6)–C(7)–C(0) for $C_{71}Cl_2$) *against the nonbonding distance* (C(7)$\cdots$C(8) for $C_{71}Cl_2$). The filled circles correspond to symmetrically bridged [10]annulenes, the open circles to symmetrically bridged [8]annulenes, and the open square to the [9]annulene found in $C_{71}Cl_2$.

The average C(7)–C(8) distance in $C_{71}Cl_2$ (2.138(1) Å) is the shortest nonbond distance found, but not by much. It is not anomalous. The bridging angle C(7)–C(0)–C(8) is also small (91.8(1)°), but the Cl(1)–C(0)–Cl(2) angle is normal (106.4(2)°).

The CSD was also searched for comparable ring systems (symmetrically CR_2-bridged C_{10} and C_8 rings composed, except at the bridgeheads, of sp^2-C-atoms.) in which there is a bond indicated between the two bridgehead C-atoms. Hits for 26 structures, 16 of them fullerenes, gave 61 distances. Comparisons of the range (1.475–1.851) and average (1.606(8)) with the values plotted in *Fig. 5* show that there is little chance of confusing bonding and nonbonding interactions. There is a gap in the observed distances from 1.85 to 2.14 Å, that is, a gap of *ca.* 0.3 Å. The longest bonded distance in a bridged fullerene is 1.70 Å, which increases the size of the gap to over 0.4 Å.

Parameters for $C_{71}Cl_2$ fit reasonably well on the curves drawn in 1975 by *Dunitz* and co-workers [7] for pericyclic ring closure in [10]annulenes with 1,6-methano bridges. The value Δ, which measures the displacement of a bridgehead C-atom (C(7) or C(8)) from the plane of its three bonded atoms (C(0), C(6), and C(21) for C(7); C(0), C(9), and C(24) for C(8)), is somewhat more negative for $C_{71}Cl_2$ (− 0.16(1) Å) than expected (*ca.* 0.00 Å), probably because of the constraints of the fullerene cage.

Crystal Packing. – The ellipsoidal fullerene molecules are arranged in double layers that extend along **a** and **b**. Each of the layers is approximately hexagonally close-packed, but is also somewhat ruffled (see *Fig. 6*). Adjacent fullerene layers are arranged so that a molecule in one layer fits into a triangular depression in the other. These double layers are separated by solvent molecules.

Within the fullerene double layers there are C ··· Cl contacts as short as 3.0 Å. While short C ··· C contacts in fullerene structures have been noted by numerous authors,

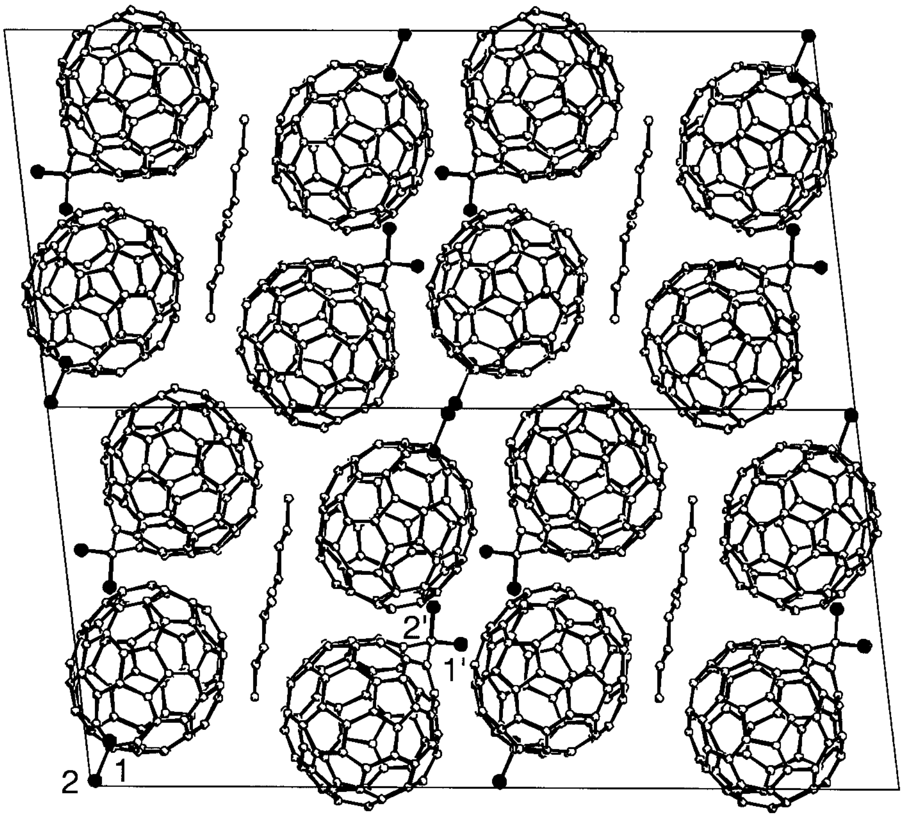

Fig. 6. *Packing diagram for two unit cells of $C_{71}Cl_2$ as observed at 110 K.* Only the pentane solvent is shown; its H-atoms have been omitted. The axis **b** points out of the plane of the paper, and **c** points from left to right. The molecule closest to the origin in the lower left of the drawing is composed of C(0) – C(70), Cl(1), and Cl(2); the other molecule is composed of C(0′) – C(70′), Cl(1′), and Cl(2′). The Cl-atoms have been darkened and labeled.

these C ⋯ Cl contacts are sufficiently unusual that we suspect they are important to the crystal packing.

In the original communication of this structure [4] we identified the Cl ⋯ Cl contacts as structure-determining, but subsequent investigation with the new CCDC program Mercury [19] and with recent versions of PLATON [13] suggests that the C ⋯ Cl contacts are more important. It appears that the basic packing unit is a tetramer located on an inversion center (*e.g.*, at 1/2,1/2,1/2). At 110 K, the intermolecular distance Cl(1′) ⋯ C(16) within that tetramer is 3.017(4) Å, *i.e.*, more than 0.4 Å shorter than the sum of the *Van der Waals* radii ($1.7 + 1.75 = 3.45$ Å) [20]. Atom Cl(1′) is also only 3.222(4) Å from atom C(34), which is bonded to C(16). On the other side of molecule 2, the distance Cl(2′) ⋯ C(33) (3.188(4) Å) is also very short. On the other hand, the Cl(1′) ⋯ Cl(2′) distance (3.612(2) Å) across the inversion center at the center of the tetramer is not really remarkable. Semi-empirical quantum-mechanical calculations for an isolated molecule were performed to see if the electron density near atoms C(16), C(34), and C(33) were especially high or low, but no significant feature was found. The existence of a tetrameric packing unit that lies on an inversion center might explain the presence in the asymmetric of two independent molecules that are not related by any obvious pseudosymmetry.

There are also short contacts between the tetramers of a fullerene double layer. At 110 K the distance Cl(1) ⋯ C(14) is 3.088(4) Å for molecules related by the **b** translation. Contacts along **a** seem to be weaker: the C(8) ⋯ C(59′) distance for atoms in tetramers adjacent along **a** is 3.182(4) Å. The Cl(1) ⋯ Cl(2) contacts (3.432(2) Å) of molecule 1 across inversion centers (*e.g.*, at 1,1/2,1/2) may also be important. There are also interactions (3.152(4) Å) between C(7′) of one tetramer and C(57) in the $C_{71}Cl_2$ molecule that lies directly over the center of that tetramer.

At 295 K, there are no short contacts between the fullerene and solvent molecules, but, as the temperature is lowered to 173 K, a C ⋯ C contact < 3.0 Å develops between a fullerene molecule and the toluene solvent molecule (occupancy 11(1)%). At 110 K, there are several such contacts, and they are impossibly short (< 2.8 Å). The significance of these very short contacts is unclear since the position of toluene molecule is not well-determined; atomic positions could easily be in error by several 0.1. Furthermore, atomic displacements of the toluene and fullerene molecules could be correlated so that the actual distances are longer than the calculated distances. On the other hand, it is possible that the thermal contraction of the crystal leaves the low-occupancy toluene molecules in a very high-energy environment. It is perhaps significant that a large fragment of the crystal split off during data collection at 110 K.

Conclusions. – Addition of a $:CCl_2$ to C_{70} gives a surprisingly normal, if somewhat constrained, methano-bridged [9]annulene. The breaking of a bond of the fullerene has few structural consequences for the rest of the C_{70} cage. Packing of the molecules in the crystal seems to be dominated by C ⋯ Cl interactions.

Experimental. – Crystals were grown by diffusion of pentane into a toluene soln. of $C_{71}Cl_2$. Data were collected with a *Nonius KappaCCD* diffractometer under control of the program Collect [21]; reflections were integrated, scaled, and corrected with Denzo-SMN [22]. Since crystals that diffracted satisfactorily were very hard to find, and since we feared the crystal might be lost at low temp., data were collected first at r.t., then at 173 K, and finally at 110 K. A substantial fragment of the crystal did break off during data collection at the lowest temp.

Since the crystal, like most fullerene crystals, scattered weakly, long count times (600 s total per frame) were used and many frames (> 445, each corresponding to a 1° scan) were measured. Data collection required 3 – 4 d at each temp. Even so, it proved impossible at r.t. to integrate reflections above $\theta = 20.7°$. Data at the two lower temp. could be integrated to 25°, but the intensities were weak ($\langle\sigma(I)/I\rangle = 0.18$; $R_{int} = 0.14$). The large number of non-H-atoms in the asymmetric unit (> 150) and the disorder of the solvent molecules account for the weak scattering; the approximately spherical arrangement of the atoms in the $C_{71}Cl_2$ molecules may also play a role. The final agreement factors are typical for carefully determined fullerene structures.

The structure was solved without difficulty with SHELXTL PC [14]; refinements used SHELXL93 [23]. After initial refinement, inspection of the peaks in a difference *Fourier* map clearly indicated the presence of a planar pentane molecule. After refinement cycles that included an isotropic C_5H_{12} molecule, the bond lengths within that molecule varied from 1.30 to 1.60 Å, and the top six peaks in a difference *Fourier* map (0.45 – 0.86 e^- $Å^{-3}$) were superimposed on the planar pentane molecule. The pattern of these remaining peaks strongly suggested a toluene molecule was also present. Final least-squares cycles included an anisotropic pentane molecule restrained to have standard bond lengths, and angles and to be planar, and an isotropic toluene molecule treated as a rigid-body. The occupancy factor was essentially constant with temp. (0.872(12), 0.892(7), 0.888(6) at 295, 173, and 110 K, resp.) as it should be since all data were collected for the same crystal. The composition of the specific crystal used is probably best described as $C_{71}Cl_2 \cdot 0.445\ C_5H_{12} \cdot 0.055\ C_7H_8$, but the ratio of the two kinds of solvent molecule might well be different in other crystals. Because the ellipsoids of the pentane C-atoms are large and are elongated within the molecular plane it seems likely that the C_5H_{12} molecules are not well-localized. The U_{iso} value for the toluene molecule decreases with T (0.100(16), 0.080(10), and 0.058(8) $Å^2$ at 295, 173, and 100 K, resp.), although not as fast as would be expected for harmonic vibrations [12].

This work was supported in part by the *MRSEC Program* of the *National Science Foundation* under Award Number DMR-9809686, and in part by the *Kentucky NSF EPSCoR* grant EPS-9452895. We also acknowledge support from the *Office of the Vice President for Research and Graduate Studies* at the University of Kentucky.

REFERENCES

[1] a) F. Wudl, *Acc. Chem. Res.* **1992**, *25*, 157; b) F. Wudl, in 'Buckminsterfullerenes', Eds. W. E. Billups, M. A. Ciufolini, VCH, New York, 1993, p. 317.

[2] F. Diederich, L. Isaacs, D. Philp, *Chem. Soc. Rev.* **1994**, *23*, 243.

[3] a) T. Nogami, M. Tsuda, T. Ishida, S. Kurono, M. Ohashi, *Fullerene Sci. Tech.* **1993**, *1*, 275; b) T. Ishida, M. Tsuda, T. Nogami, S. Kurono, M. Ohashi, M., *Fullerene Sci. Tech.* **1994**, *2*, 155; c) M. Tsuda, T. Ishida, T. Nogami, S. Kurono, M. Ohashi, *Tetrahedron Lett.* **1993**, *34*, 6911.

[4] A. F. Kiely, R. C. Haddon, M. S. Meier, J. P. Selegue, C. P. Brock, B. O. Patrick, G.-W. Wang, Y. Chen, *J. Am. Chem. Soc.* **1999**, *121*, 7971; A. F. Kiely, R. C. Haddon, M. S. Meier, J. P. Selegue, C. P. Brock, P. O. Patrick, G. W. Wang, Y. Chen, *J. Am. Chem. Soc.* **2000**, *122*, 4845.

[5] M. J. van Eis, P. Seiler, L. A. Muslinkina, M. Badertscher, E. Pretsch, F. Diederich, R. J. Alvarado, L. Echegoyen, I. P. Núñez, *Helv. Chim. Acta* **2002**, *85*, 2009.

[6] B. B. Iversen, A. Darovsky, R. Bolotovsky, P. Coppens, *Acta Crystallogr., Sect. B* **1998**, *54*, 174.

[7] H. B. Bürgi, E. Shefter, J. D. Dunitz, *Tetrahedron* **1975**, *31*, 3089.

[8] M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **1996**, *118*, 3775.

[9] E. W. Godly, R. Taylor, *Pure Appl. Chem.* **1997**, *69*, 1411.

[10] W. H. Powell, F. Cozzi, G. P. Moss, C. Thilgen, R. J.-R. Hwu, A. Yerin, *Pure Appl. Chem.* **2002**, *74*, 629.

[11] P. Seiler, A. Herrmann, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 344.

[12] a) J. D. Dunitz, V. Schomaker, K. N. Trueblood, *J. Phys. Chem.* **1988**, *92*, 856; b) J. D. Dunitz, E. F. Maverick, K. N. Trueblood, *Angew. Chem. Int. Ed.* **1988**, *27*, 880.

[13] A. L. Spek, PLATON, 2002, Utrecht University, The Netherlands.

[14] G. M. Sheldrick, SHELXTL PC, Release 4.1, 1990, *Siemens Analytical Instruments, Inc.*, Madison, Wisconsin.

[15] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

[16] A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123.

[17] H. Irngartinger, C.-M. Koehler, G. Baum, D. Fenske, *Liebigs Ann. Chem.* **1996**, 1609.
[18] H. B. Bürgi, P. Venugolpalan, D. Schwarzenbach, F. Diederich, C. Thilgen, *Helv. Chim. Acta* **1993**, *76*, 2155.
[19] R. Taylor, C. F. Macrae, *Acta Crystallogr., Sect. B* **2001**, *B57*, 815.
[20] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[21] R. Hooft, KappaCCD Collect Software, 1998, Nonius BV, Delft, The Netherlands.
[22] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[23] G. M. Sheldrick, 'SHELXL93: Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1993.

Received February 4, 2003