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C_1 $C_{70}F_{38}$ Contains Four Planar Aromatic Hexagons; The Parallel between Fluorination of [60]- and [70]Fullerenes

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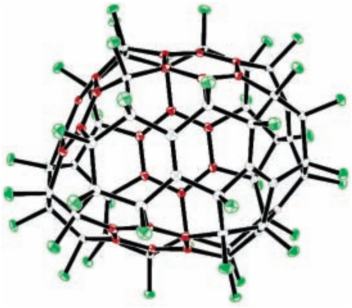
ABSTRACT



The main C_1 isomer of $C_{70}F_{38}$ is shown by single-crystal X-ray analysis to contain four planar aromatic hexagons and four isolated C=C bonds, has two fluorines on the equator, and is related to C_2 $C_{70}F_{38}$ by means of three 1,3-fluorine shifts. The C_1 and C_2 isomers thus parallel the T and C_3/C_1 isomers of $C_{60}F_{36}$ in containing three and four aromatic rings, respectively, and in the fluorine shift relationship.

There has been a recent upsurge in interest in the polyaddition of [70]fullerene, with hitherto unsuspected patterns being revealed. For example, reaction with *tert*-butylperoxy radicals[1] gave not only the 10-fold addition pattern seen previously in many reactions[2] but also a C_s 6-fold (cyclopentadienyl) addition pattern[3] found until now only in reactions of [60]fullerene. Troyanov et al.[4] reported very recently the X-ray characterization of $C_{70}Cl_{28}$ showing this derivative to contain four aromatic rings, being a mixture of three isomers related by a series of 1,5-shifts of chlorine. These isomers contain up to nine contiguous chlorine atoms, a steric crowding situation that would formerly have been considered very unlikely. This incipient destabilization is evidently counterbalanced here by the presence of the four aromatic rings.

Simultaneously we reported[5] the single-crystal X-ray characterization of the C_2 symmetric isomer of $C_{70}F_{38}$, one of the two main isomers that had been identified in earlier work[6] (but not then characterized fully because of the sample size and complexity of the ^{19}F NMR spectrum). This C_2 isomer contains three planar aromatic rings, thereby providing the evidence to support earlier conjectures[7,8] that the specific 36 and 38 addition levels in hydrogenation[9] (iso-

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structural with fluorination)[10] are due to the formation of benzenoid patches.

Clare and Kepert calculations of the stabilities of $C_{70}X_{36/38}$ (X = both H and F) indicated these to be aromatic,[11] though MNDO calculations predicted that nonaromatic structures would, for steric reasons, be much more stable.[12] In both calculation sets, structures having addition at any of the 10 equatorial carbons (at the conjunction of three hexagons) were predicted to be improbable as a result of introduction of unacceptable strain. A surprising feature of the structure of C_2 $C_{70}F_{38}$ (**14**)[5,6] therefore was the presence of addends on equatorial carbons, a hitherto unknown feature of [70]-fullerene chemistry. It appears that, as in the case of $C_{70}Cl_{28}$, strain is compensated by an increase in aromaticity.

We have now succeeded in obtaining from toluene a crystal of the other main isomer (**8**)[6] of $C_{70}F_{38}$, suitable for X-ray analysis, and produced by the fluorination conditions described previously.[5] Separation of the products by HPLC (high-pressure liquid chromatography) gave this isomer in a yield comparable with that of **14**; no other components gave suitable crystals. The single-crystal X-ray structure (Figure 1)[13] reveals the structure to be aromatic, having *four* planar delocalized benzenoid rings (shown in red), together with four isolated double bonds. Thus just as $C_{60}F_{36}$ comprises isomers containing three (C_1, C_3) and four (T) aromatic rings,[14,15] so $C_{70}F_{38}$ behaves similarly. Moreover, the isomers are similarly related by a series of 1,3-fluorine shifts (see below).

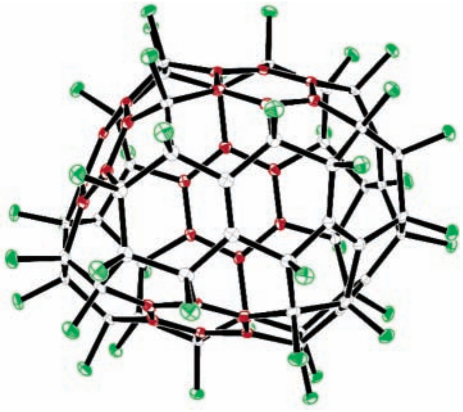

Figure 1. ORTEP drawing (20% ellipsoids) for C_1 $C_{70}F_{38}$ (isomer **8**) with aromatic rings shown in red and fluorine atoms in green; the central facing C=C bond is C20−C21 (see Figure 2b).

The aromatic rings for this isomer are also highlighted in red in the Schlegel diagram (Figure 2b), which is shown for comparison with the corresponding diagram for the C_2 isomer **14** (Figure 2a). (Because isomers **8** and **14** are structurally related, in Figure 2b we have exceptionally and for consistency not used the IUPAC lowest locant rule, which would if applied, make carbons 56, 57, 68, 67, etc. = nos. 1, 2, 3, 4, respectively.)

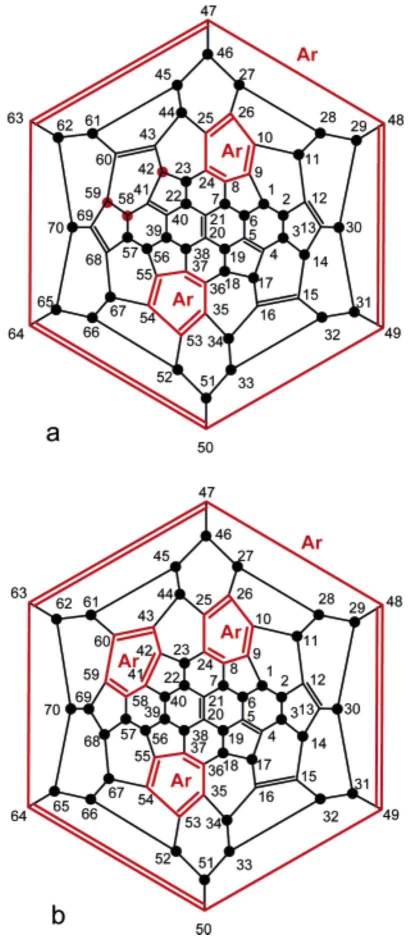

Figure 2. Schlegel diagrams for C_2 and C_1 $C_{70}F_{38}$, respectively; ● = F; the red circles are fluorines that are 1,3-shifted in (a) to give (b) (see text).

As in the case of the C_2 isomer, there are two fluorine atoms located on the equator, the destabilization introduced by this evidently being overcome by the aromaticity of the

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(13) Crystal data: $C_{70}F_{38}\cdot(C_7H_8)$, MW = 1654.83 monoclinic, space group $P2_1/c$ (No. 14), a = 13.1882(6), b = 20.6428(7), c = 20.0742(10) Å, β = 91.711(2), V = 5462.6(4) Å^3, Z = 4, D_x = 2.01 Mg·m^{-3}, μ(Mo Kα) = 0.21 mm^{-1}, T = 173(2) K. The toluene solvate molecule is disordered and was included with rigid body C6 rings and isotropic C atoms; 9509 unique reflections (R_{int} = 0.043) measured on a KappaCCD diffractometer. Refinement on F^2 using SHELXL-97, R1 = 0.052 for 6918 reflections with $I > 2\sigma(I)$, wR2 = 0.131 for all reflections. CCDC ref no. 257567.

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structure. The equatorial atoms are nos. 20, 21, 24, 25, 35, 36, *46*, 47, 50, and *51*, the addended carbons being italicized. The locations of these fluorines is apparent from Figure 2a,b.

The Schlegel diagrams (Figure 2a,b) show in detail how isomer **8** is related to isomer **14** by virtue of three 1,3-shifts of fluorine atoms (shown as filled red circles), viz. 42 → 40, 59 → 68, and 58 → 69, paralleling the relationships between the isomers of $C_{60}F_{36}$.[9,10] It would be reasonable to suppose that an equivalent set of rearrangements could occur to give a further aromatic ring composed of carbons 3, 4, 14, 15, 16, and 17, giving another C_2 symmetry product **X** (Figure 3) having five aromatic rings.

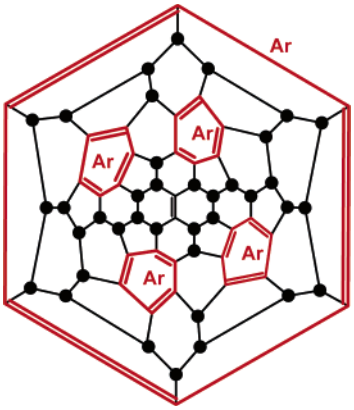

Figure 3. Schlegel diagram of conjectured structure (isomer **X**) that would arise from three further 1,3-fluorine shifts paralleling those producing isomer **8** from isomer **14** (see text).

Since we found no evidence for the existence of this isomer, the stabilities of **14**, **8**, and **X** were investigated theoretically. Semiempirical calculations used the AM1 Hamiltonian[16] as implemented in the program MOPAC.[17]

At a higher level of theory, local density functional calculations were performed using the AIMPRO code[18] in the cluster approach. The exchange-correlation functional used is the PADE approximation[19] to the Perdew-Wang 92 functional.[20] Pseudopotentials (see ref 21) were used with the energy cutoff of 350 Ry. Wave functions were expanded in basis sets consisting of atom-centered Gaussian orbital functions (s and p for C; s, p and d for F) with four independently varied exponents per atom.

The relative stabilities (kcal mol^{-1}) of these 3-, 4- and 5-aromatic ring structures are predicted, respectively, as 0, 10.5, 22.6 (AM1); 0, −11.9, −12.6 (DFT). Thus isomer **14** is predicted to be less stable than isomer **8** according to AM1 but more stable by DFT. Isomer **X** should be isolable according to DFT but unlikely to exist according to AM1. Note that calculations by Clare and Keppert of the relative stabilities of $C_{60}X_{36}$ isomers (X = H, F) also showed different orders between AM1 and DFT methods.[22] They observed that DFT calculations favor structures with aromatic rings, whereas AM1 favors structures with isolated double bonds. Despite a different DFT technique being used in our work, the same trend is apparent: structures with four or five aromatic rings (isomers **14** and **X**) are predicted to be more stable by DFT calculations and less stable by AM1.

Correlation of the observed C−C bond lengths for C_1 $C_{70}F_{38}$ with those calculated is good [average deviation of 0.018 Å (AM1) and 0.009 Å (DFT)], the latter being more indicative of the relevant ring aromaticities.

The average bond lengths (Å) in the four aromatic rings of isomer **8** (Table 1), viz., 1.387(5), 1.385(5), 1.370(5), and 1.379(5), confirm their aromaticity. Compare the values found in C_1 $C_{60}F_{36}$ (1.371, 1.378, 1.389),[14] T $C_{60}F_{36}$,[23] and $C_{60}F_{18}$[24] (both 1.373); values of the three rings in isomer **14**

Table 1. Cage C−C Bond Lengths (Å)[a] for C_1 $C_{70}F_{38}$

bond	length	bond	length	bond	length
1−2	1.593	21−22	1.512	44−45	1.598
1−6	1.571	22−23	1.608	45−46	1.577
1−9	1.501	22−40	1.600	45−61	1.651
2−3	1.573	23−24	1.521	46−47	1.494
2−12	1.530	23−42	1.490	47−48	1.377
3−4	1.495	24−25	1.419	47−63	1.385
3−14	1.561	25−26	1.387	48−49	1.375
4−5	1.320	25−44	1.517	49−50	1.381
4−17	1.503	26−27	1.497	50−51	1.484
5−6	1.488	27−28	1.634	50−64	1.390
5−19	1.505	27−46	1.567	51−52	1.552
6−7	1.581	28−29	1.559	52−53	1.486
7−8	1.498	29−30	1.568	52−66	1.645
7−21	1.535	29−48	1.487	53−54	1.374
8−9	1.373	30−31	1.580	54−55	1.373
8−24	1.393	31−32	1.529	54−67	1.483
9−10	1.371	31−49	1.488	55−56	1.469
10−11	1.489	32−33	1.635	56−57	1.545
10−26	1.378	33−34	1.581	57−58	1.485
11−12	1.498	33−51	1.595	57−68	1.652
11−28	1.568	34−35	1.501	58−59	1.367
12−13	1.326	35−36	1.400	59−60	1.395
13−14	1.493	35−53	1.397	59−69	1.487
13−30	1.494	36−37	1.385	60−61	1.479
14−15	1.520	37−38	1.502	61−62	1.538
15−16	1.317	37−55	1.378	62−63	1.490
15−32	1.512	38−39	1.583	62−70	1.633
16−17	1.504	39−40	1.566	63−64	1.364
16−34	1.493	39−56	1.641	64−65	1.492
17−18	1.558	40−41	1.488	65−66	1.545
18−19	1.581	41−42	1.374	65−70	1.587
18−36	1.512	41−58	1.388	66−67	1.568
19−20	1.529	42−43	1.380	67−68	1.574
20−21	1.335	43−44	1.487	68−69	1.597
20−38	1.513	43−60	1.375	69−70	1.567

[a] Esd values are all 0.005 ± 0.001 Å.

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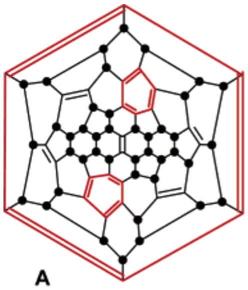
were 1.381(5), 1.384(5), and 1.382(5).[5] The lengths of the C12−C13, C20−C21, and C15−C16 bonds are virtually identical to those of the corresponding bonds in isomer **14**, the latter exceptionally short bond being attributed to compression effects.[5] The C4−C5 bond (1.320 Å) is notably shorter than the corresponding bond (1.343 Å) in isomer **14**.

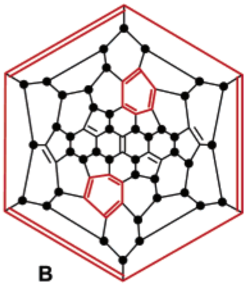
Whereas in the C_2 isomer there was one exceptionally long FC−CF bond of 1.642 Å (C27−C28/C52−C66), here there are no less than eight, having an average length of 1.640 Å, and all are found where one of the participating carbons has three CF neighbors. This implies greater steric strain in the C_1 isomer and probably accounts for the failure to find a C_2 isomer having five benzenoid rings. The planarity of the benzenoid rings is indicated by the sums of the valence angles for the carbons, which comprise the aromatic rings. These are 358.1°, 358.6°, 359.3°, and 359.7° for each of the aromatic rings, cf. the 360° ideal.

There are six carbons (nos. 28, 33, 45,66, 68, 70) with three CF neighbors, giving rise to six upfield multiplets in the ^{19}F spectra, as observed.[6] It may subsequently be possible to assign all of the spectrum peaks and to interpret the structures of the other fluorinated C_{70} derivatives for which good NMR spectra were obtained; a significant feature is that some peaks for spectra run in toluene/$CDCl_3$ showed significant shifts relative to those obtained in $CDCl_3$ alone.

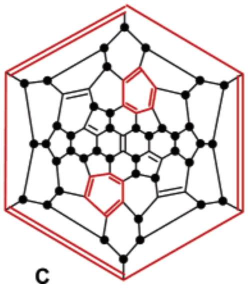
A feature of the NMR spectra of the range of other fluorinated [70]fullerenes[6] noted briefly here is the C_s or (most probably) C_2 symmetry of the isolated $C_{70}F_{42}$. Given the structure of the C_2 isomer of $C_{70}F_{38}$, it is probable that the isomer of $C_{70}F_{42}$ is related by the addition of two pairs of fluorine atoms across equivalent pairs of double bonds. This would give structures **A**−**C**. Calculations of the relative energies (kcal mol^{-1}) of **A**, **B**, and **C** are 0, −12.1, −9.0 (AM1); 0, −25.4, −14.3 (DFT cluster). Both methods are in agreement that **B** is the most stable and **A** the least stable, and this may aid subsequent and detailed solution of the ^{19}F NMR spectrum.



A



B



C

Five isomers of $C_{70}F_{40}$, all C_1, were isolated previously.[6] Addition of a pair of fluorines to any double bond in either of the C_2 or C_1 isomers of $C_{70}F_{38}$ would give seven possible products, all of them C_1. This approach may similarly provide a means to eventual solution of these $C_{70}F_{40}$ structures, especially since our current investigations indicate that no further crystalline derivatives will be isolated.

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