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Structural Analysis of Products from the C_{60}–Piperazine Reaction. Consistent Geometric Distortions of the Fullerene Core Upon Adduct Formation.

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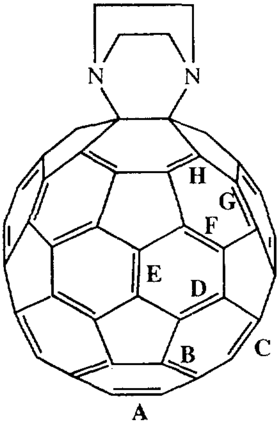
Abstract. The reaction of C_{60} with piperazine yields the single addition product, $C_{60}N_2(C_2H_4)_2$, and six double addition products which can be chromatographically separated. Of these, single crystal X-ray diffraction characterization has produced structural data for the identification of $(C_2H_4)_2N_2C_{60}$ and three isomeric forms of the double addition product, $\{(C_2H_4)_2N_2\}_2C_{60}$. Addition of the $N_2(C_2H_4)_2$ units produces local distortions of the fullerene core which involve marked elongation of the C–C bond at the 6:6 ring junction that is involved in the addition and outward displacement of these carbons from their usual positions by ca 0.33–0.40 Å. The combined effects of double addition can produce local distortions that appear visually more severe but which retain the structural features found in the single addition product.

Introduction.

C_{60} reacts with amines to from adducts whose structural characterization has been impeded by the array of different products that form.[1-8] The reaction with diamines like piperazine has the advantage of forming products that can be separated and purified.[4,6-8] These products consist of materials in which one or two molecules of the diamine add to the fullerene with the unanticipated loss of two or four hydrogen atoms. Initially this project was undertaken to verify that these hydrogen atoms were not incorporated into the fullerene core in some fashion. We recently reported on the structural and electrochemical characterization of the single addition product, $(C_2H_4)_2N_2C_{60}$, and of one isomeric form of the double addition products, $\{(C_2H_4)_2N_2\}_2C_{60}$, that are formed in this reaction.[8] The structure of $(C_2H_4)_2N_2C_{60}$ shows that the amine has added across a 6:6 ring junction of the fullerene. If further reactions also occur at 6:6 ring junctions, then there are eight possible double addition products that can form. These are shown graphically in Chart I, where the maximal symmetry of each isomer is given. With additions of this sort, there is the question of the degree of distortion that the fullerene core can accommodate. This is especially interesting with multiple additions where one might expect significant alteration to the fullerene core. Here we report on the structure of two more isomeric forms of $\{(C_2H_4)_2N_2\}_2C_{60}$ that have been isolated and purified from the piperazine/C_{60} reaction.

Chart I. Isomeric Forms of $\{(C_2H_4)_2N_2\}_2C_{60}$



Site	Maximum Symmetry
H	C_s
G	C_s
F	C_2
E	C_s
D	C_s
C	C_2
B	C_2
A	D_{2h}

Results.

Adduct Preparation and Separation. The reaction of C_{60} with piperazine was performed under the conditions originally reported by Kampe *et al.*[4,6] The mixture of adducts that were obtained was analyzed by high pressure liquid chromatography (HPLC) with the use of a "Buckyclutcher" column[9] and 9/1 dichloromethane/methanol as eluent. Figure 1 shows a typical HPLC trace which reveals that seven distinct bands due to the adducts are observed.

The material from each of these peaks was collected and then purified by subsequent chromatography using the same system. Material in peaks labeled a, b, c and f has been induced to form crystals suitable for study by single crystal X-ray diffraction. The material in peak a is $1,2\text{-}(C_2H_4)_2N_2C_{60}$ and that in c is the double addition product, isomer **B** of $\{(C_2H_4)_2N_2\}_2C_{60}$, as reported previously.[8] As shown in the following sections the material in peak b is isomer **G**, and the material in peak f is isomer **E**.

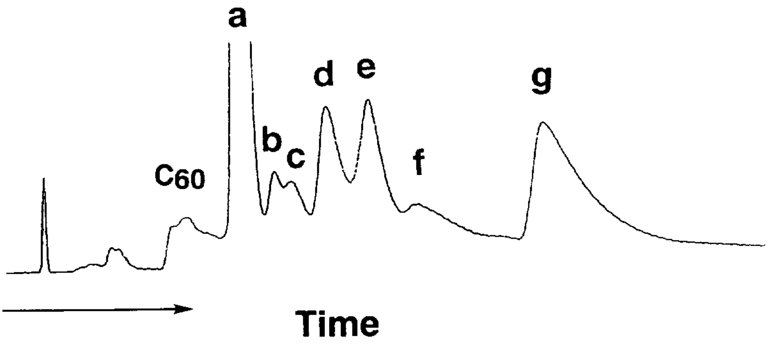


Figure 1. HPLC trace of the toluene solution from the C_{60}/piperazine reaction. Flow rate, 2.0 mL/min., solvent 9/1 dichloromethane/methanol, monitoring wavelength, 425 nm.

Distortions in $(C_2H_4)_2N_2C_{60}$ In order to visualize the effects of adduct formation on the fullerene geometry, Figure 2 presents a view of $(C_2H_4)_2N_2C_{60}$ onto which the structure of an idealized C_{60} molecule has been superimposed. The ideal C_{60} molecule used has I_h symmetry and C–C bond lengths of 1.383 Å at the 6:6 ring junctions and 1.453 Å at the 5:6 ring junctions. These values were taken from the average values found in the X-ray crystal structure of a well-ordered fullerene; C_{60}•$3SbPh_3$.[10] The position of the ideal fullerene is shown by dashed lines while the location of $(C_2H_4)_2N_2C_{60}$ is shown with solid lines. Notice that for most of the drawing the dashed and solid lines cannot be visually differentiated. However, in the vicinity of C(1) and C(2) there are detectable differences. The following effects of adduct formation occur and alter the fullerene core geometry. The C(1)–C(2) bond distance is elongated to 1.624(8) Å. The four other bonds that involve C(1) and C(2) are lengthened from the normal distance of 1.453 Å to values of 1.532 (10), 1.537 (8), 1.531 (8) and 1.533 (8) Å. The quaternary carbons, C(1) and C(2) are displaced outwardly by 0.345 and 0.365 Å. Additionally there has been outward movement of the carbon atoms in the hexagons adjacent to the site of addition by 0.015 to 0.040 Å. For comparison, the weighted rms deviations in location of the other carbon atoms of the adduct and the ideal C_{60} is 0.020 Å.

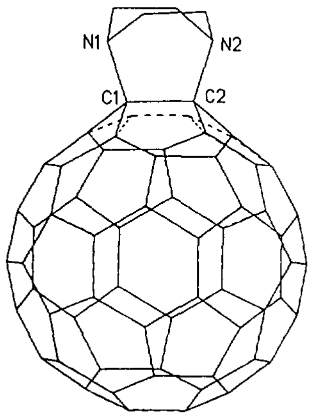


Figure 2. Superimposed diagrams of $(C_2H_4)_2N_2C_{60}$ (solid lines) and idealized C_{60} (dotted lines) which show the local distortion of the fullerene that accompanies adduct formation.

Structure of Isomer G of $\{(C_2H_4)_2N_2\}_2C_{60}$. The material in peak b of the chromatogram in Figure 1 contains isomer G of $\{(C_2H_4)_2N_2\}_2C_{60}$. There are two molecules of this adduct and a molecule of diethyl ether in the asymmetric unit. Figure 3 shows a perspective

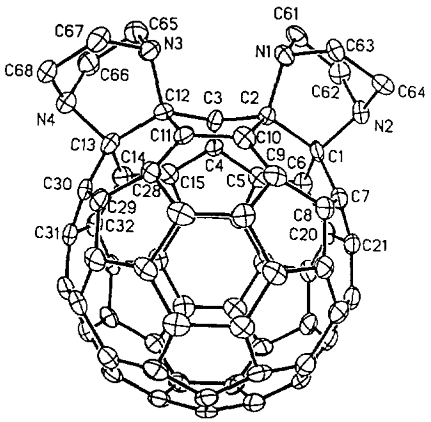


Figure 3. A perspective drawing of isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$, with 50 % thermal contours.

drawing of one of the two modified fullerene molecules. The individual molecules do not have any crystallographically imposed symmetry; however they do have idealized C_s symmetry. The virtual mirror plane is perpendicular to the plane of the drawing in Figure 3 and bisects C(3) and C(4). Figure 4 shows a view of a portion of the molecule which emphasizes the relative orientations of the amine portion and their proximity. The non-bonded N(1)-N(2) and N(3)-N(4) distances within the amine cages are 2.570 and 2.571 Å (2.607 and 2.580 Å in molecule 2) while the longer N(1)-N(3) distance is 3.276Å (3.284 Å in molecule 2).

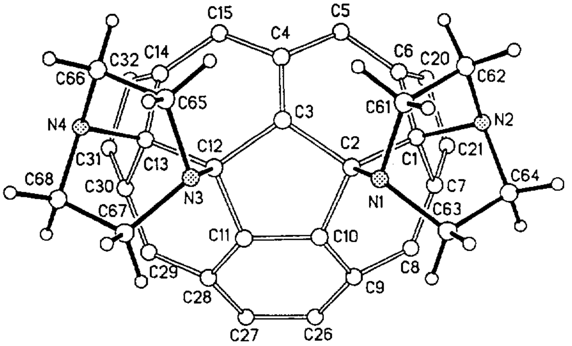


Figure 4. A drawing of a portion of isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ from a perspective that emphasizes the relative orientations of the two amine functions.

Both of the two molecules of the modified fullerene have very similar geometries. When the two structures are compared, the weighted rms deviation of all atoms is only 0.0340 Å. For the fullerene portion, the atomic positions differ from 0.007Å to 0.050 Å, while larger deviations are found for the more flexible portion that was derived from piperazine. There the deviations range from 0.030Å to 0.086 Å.

As Figure 3 shows, visually there is some distortion of the fullerene in the vicinity of the site of adduct formation. For example the five-membered ring that contains C(12), C(3) and C(2) is no longer planar but is bent outward. As expected from results on the single addition product, $(C_2H_4)_2N_2C_{60}$, the bond lengths between the quaternary carbons are elongated. The C(1)–C(2) distance is 1.628(9) Å and the C(12)–C(13) distance is 1.624(9) Å. (In molecule 2 these distances are 1.650 (11) and 1.590 (10).) Nevertheless the distortions observed are analogous to those seen in the single addition product, $(C_2H_4)_2N_2C_{60}$. Figure 5 presents a view of isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ onto which is superimposed the structure of an ideal C_{60} molecule. It is readily apparent that the majority of the fullerene carbon atoms retain their normal positions in the adduct, but that C(1), C(2), C(12) and C(13) are significantly shifted away from the surface as are the analogous quaternary carbon atoms in $(C_2H_4)_2N_2C_{60}$. In isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ the outward displacements of these carbon atoms are: C(1), 0.350 Å; C(2), 0.362 Å; C(12), 0.378 Å; and C(13), 0.361 Å. In the second molecule the corresponding displacements are 0.350, 0.399, 0.375, and 0.343 Å. For comparison for the 44 carbon atoms that are not affected by the adduct formation the weighted rms deviation is 0.0241 Å.

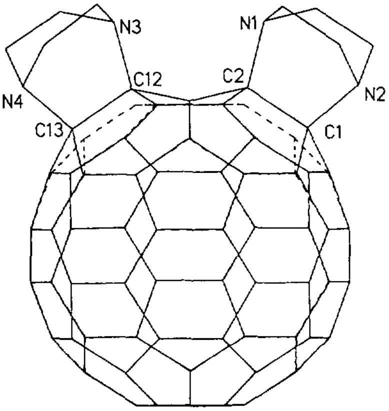


Figure 5. Superimposed diagrams of isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ (solid lines) and idealized C_{60} (dotted lines) which show the local distortion of the fullerene that accompanies adduct formation.

Structure of Isomer E of $\{(C_2H_4)_2N_2\}_2C_{60}$. The crystalline material that was obtained from peak f contains isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$. The crystalline solid contains two molecules of the addition product and a molecule of dichloromethane in the asymmetric unit. Figure 6 shows a drawing of one of the two independent adduct molecules. The other is virtually identical. The two structures can be superimposed upon one another to give a weighted rms deviation for all atoms of only 0.0286 Å. The largest deviations are found within the amine and ethylene portions where the deviations range from 0.025 Å to 0.088 Å. Within the fullerene portion the deviations range from 0.005 Å to 0.038 Å. These adducts do not have crystallographically imposed symmetry but there is a virtual mirror plane which passes through N(3), N(4), C(16) and C(34).

As Figure 6 shows, there is a noticeable distortion of the fullerene core so that the portion of the fullerene on the top part has a flattened shape that contrasts markedly with the normal, curved shape on the bottom of this figure. The distortion on the top part is particularly pronounced because there is a concave five-membered ring fused to a concave six-membered ring at this site. Nevertheless the distortions of the fullerene are still similar to those present in

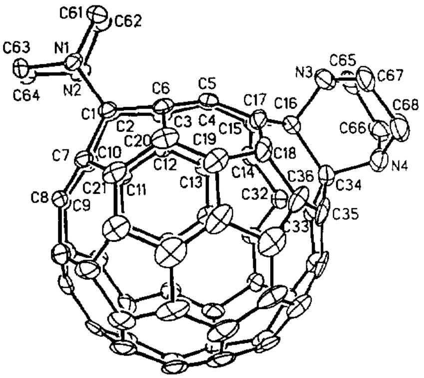


Figure 6. A perspective drawing of isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$ with 50 % thermal contours.

the single addition product, $(C_2H_4)_2N_2C_{60}$. Figure 7 shows a comparison of the structure of isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$ with that of an ideal molecule of C_{60}. The format is the same as used in Figures 2 and 5. As one can see, major deviations are localized in the vicinity of the sites of addition and involve primarily the outward displacement of the quaternary carbon atoms and the elongation of the bonds between these atoms. The C(1)-C(2) distance is 1.583 (8) Å and the C(16)-C(34) distance is 1.620 (9) Å. In molecule 2 these distances are 1.604(8) and 1.618 (8) Å. The outward displacements of these carbon atoms are: C(1), 0.341 Å; C(2), 0.349 Å; C(16), 0.331 Å; and C(13), 0.328 Å. In the second molecule the corresponding values are: 0.351,

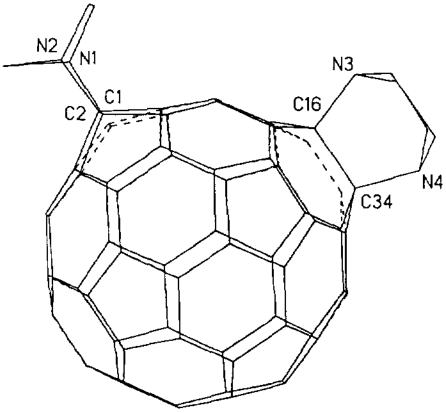


Figure 7. Superimposed diagrams of isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$ (solid lines) and idealized C_{60} (dotted lines) which show the local distortion of the fullerene that accompanies adduct formation.

0.363, 0.338, and 0.319 Å. For comparison for the 34 carbon atoms that are not affected by the adduct formation the weighted rms deviation in fullerene carbon atom locations is 0.017 Å (0.18 Å for the second molecule.).

Discussion.

At this stage three of the possible eight isomers of $\{(C_2H_4)_2N_2\}_2C_{60}$ have been structurally characterized. Examination of Figure 4 reveals that there are no unusual contacts between the two amine addenda in isomer **G** which has these groups closer together than isomers **E** or **B**. However the sizes of these groups are such that it is not possible to form isomer **H** without severe contacts between the piperazine derived portions of the adducts. Consequently it is unlikely that isomer **H** of $\{(C_2H_4)_2N_2\}_2C_{60}$ will ever exist. In contrast, it should be noted that isomers **H** of both $C_{60}H_4$[11] and of $C_{60}O_2$[12] are the most readily formed of any of the isomers with these compositions. However, there do not appear to be any steric factors that would inhibit the formation of any other isomers of $\{(C_2H_4)_2N_2\}_2C_{60}$.

The results presented here show that the formation of the adducts in the C_{60}-piperazine reaction results in a rather consistent set of modifications of the core geometry of the fullerene. Figure 8 shows a pyracylene portion of a fullerene. The dimensions given there are the averages for (virtual) symmetry related groups. The two nitrogen atoms are attached to the two central carbon atoms. The structures of $(C_2H_4)_2N_2C_{60}$ and of isomers **E** and **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ were used to obtain the data for the following analysis. The crystallographic data for isomer **B** is

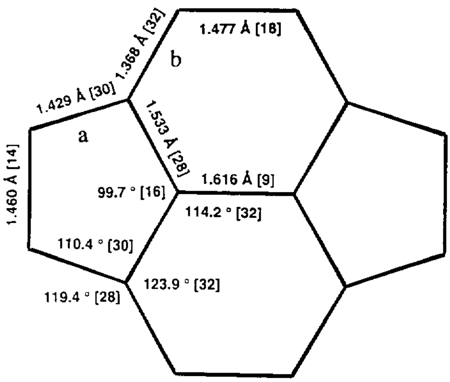


Figure 8. A diagram of the pyracylene portion of C_{60} to which a $(C_2H_4)_2N_2$ group has been added. The bond distances and angles are average values. The numbers in brackets are the number of independent measurements that are involved in the average.

less accurate and was not included. The values in brackets in Figure 8 are the number of independent observations used to obtain the average bond distances or angles. There are a number of modifications to the fullerene core which occur. There is marked elongation of the fullerene C-C bond to which the amine nitrogen atoms are attached. This lengthening produces a very long C-C bond which approaches the longest C-C bond length known.[13] Related elongation of C-C bonds within fullerenes has also been observed in the formation of Diels-Alder adducts,[14] 2+2 cycloadducts,[15] and nitrile oxide adducts.[16] The four C-C bonds that surround the two quaternary carbon atoms are also lengthened to 1.553 Å from the normal value of 1.453 Å. The bonds denoted as a and b in Figure 8 are slightly shorter than normal. In addition to the bond length changes the two quaternary carbon atoms undergo outward displacement by an average of 0.37 Å upon adduct formation, and the carbon atoms in the hexagons that are adjacent to the site of addition also show small outward displacements .

Isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ appears to be organized so that it should be able to chelate metal ions between N(1) and N(3). A metal ion with an M-N bond length of 2.1 Å would fit snugly between these two nitrogen atoms. The resulting N-M-N angle would be 102 °.

Experimental Section

Adduct Preparation and Separation. Following the procedure of Kampe *et al.*[4,6] under a dinitrogen atmosphere, a solution of 287 mg (3.33 mmol) of piperazine in 20 mL of toluene was added to a solution of 200 mg (0.278 mmol) of C_{60} in 150 mL of toluene. The mixture was stirred and heated at 50°C for 5 days. During this period the solution changed from magenta to reddish purple after two days and became yellowish brown by the end of the third day. After cooling the mixture and filtration, aliquots of the filtrate were separated on an automated Waters 746 HPLC unit. The mobile phase was 9:1 dichloromethane:methanol. A 0.30 mL sample of the filtrate was injected, and a flow rate of 2.0 mL/min was used. Figure 1 shows a typical chromatographic profile. Fractions from peaks a-f were collected separately and those from multiple injections were combined. The solvent from each peak was removed by vacuum evaporation. The material from each peak was then redissolved in a minimum volume of toluene and subjected to a second round of chromatography, collected and evaporated to dryness. This procedure was repeated a third time. The yields of the products at this stage were: $\{(C_2H_4)_2N_2\}_2C_{60}$ from peak a, 20 mg, 10 %; isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ from peak b, 3 mg, 1.5 %; isomer **B** of $\{(C_2H_4)_2N_2\}_2C_{60}$ from peak c, 2 mg, 1 %; and isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$ from peak f, 4 mg, 2 %. These samples were eventually induced to form crystals suitable for single crystal X-ray diffraction. Although crystallization of the material in peaks d, e, and g has been attempted, none of these has yet produced suitable crystals. Kampe *et al.* have reported[4,6] that they were able to separate six isomeric forms of $\{(C_2H_4)_2N_2\}_2C_{60}$

through column chromatography on a larger quantity of material than we have used. When we attempted to interface our results with theirs, it appeared that comparison of R_f values for chromatography on silica gel with 10/1 dichloromethane/ethanol as eluent would be informative; since these values offered the most distinctive characteristics reported in reference 6. However while Kampe *et al.*[4,6] reported R_f values in the range 0.46 -0.10 for their products, we have observed a different range of values. For peaks b, c, d, e, and f in Figure 1, we found R_f values of 0.95, 0.85, 0.48, 0.46 and 0.46, respectively. Because of the differences in our results, it is not possible for us to propose an identification of the materials in the chromatographic separation reported in reference 6.

X-ray Data Collection. Crystals of isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ were obtained by diffusion of diethyl ether into a solution of the compound in dichloromethane. A suitable crystal was coated with a light hydrocarbon oil and mounted in the 123(2) K dinitrogen stream of a Siemens P4/RA diffractometer that was equipped with a LT-2 low temperature apparatus. Intensity data were collected with nickel-monochromated CuKα radiation (λ = 1.54178 Å). Two check reflections showed only random (< 2%) variation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are presented in Table 1.

Crystal of isomer **E** of $\{(C_2H_4)_2N_2\}_2C_{60}$. were obtained through the slow diffusion of diethyl ether into a 9:1 dichloromethane:methanol solution of material that was obtained from peak f during the chromatographic separation. A suitable crystal was handled and data collected as described above. Three check reflections showed 2.3% decay in intensity during data collection. The data were corrected for Lorentz, polarization, and decay effects. Further details are given in the Supplementary Material.

Solutions and Refinements of the Structures. Calculations were performed with SHELXTL Plus (Sheldrick, Siemens, 1995). Scattering factors and corrections for anomalous dispersion were taken from a standard source.[17] Both structures were solved by use of the mono-adduct as a fragment for rotation search in the space group P1 followed by location of the correct origin and transformation of the coordinates back to the correct space group.[18] Hydrogen atoms were fixed to appropriate carbon atoms though the use of a riding model with a fixed, isotropic U. For isomer **G** of $\{(C_2H_4)_2N_2\}_2C_{60}$ the largest peak and hole in the final difference map had a values of 0.385 and -0.363 eÅ^{-3}. For isomer **E** of$\{(C_2H_4)_2N_2\}_2C_{60}$, one reflection (2,0,0) was omitted because of extinction. The largest peak and hole in the final difference map had values of 0.334 and -0.471 eÅ^{-3}.[19]

Acknowledgments. We thank the National Science Foundation (Grant CHE 9321257) for financial support.

Table 1. Crystal Data for Fullerene Addition Products

Compound	Isomer **G**, $\{(C_2H_4)_2N_2\}_2C_{60}$ •0.5 $(C_2H_5)_2O$	Isomer **E**, $\{(C_2H_4)_2N_2\}_2C_{60}$ •0.5 CH_2Cl_2
Formula	$C_{70}H_{21}N_4O_{0.50}$	$C_{68.5}H_{17}ClN_4$
Formula Weight	925.91	931.31
Crystal System	orthorhombic	orthorhombic
Space Group	$P2_12_12_1$	Pbca
a/Å	9.9930(10)	19.837(4)
b/Å	22.968(5)	17.798(4)
c/Å	32.099(5)	40.583(8)
V/Å^3	7367(2)	14328(5)
D_x/Mgm^{-3}	1.670	1.727
Z	8	16
No. Unique Reflections	5380	9010
No. Observed Reflections [$I > 2\sigma(I)$]	4568	5780
No Parameters	1344	1324
R1 [Observed refls]	0.052	0.064
wR2 [All refls]	0.135	0.196

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