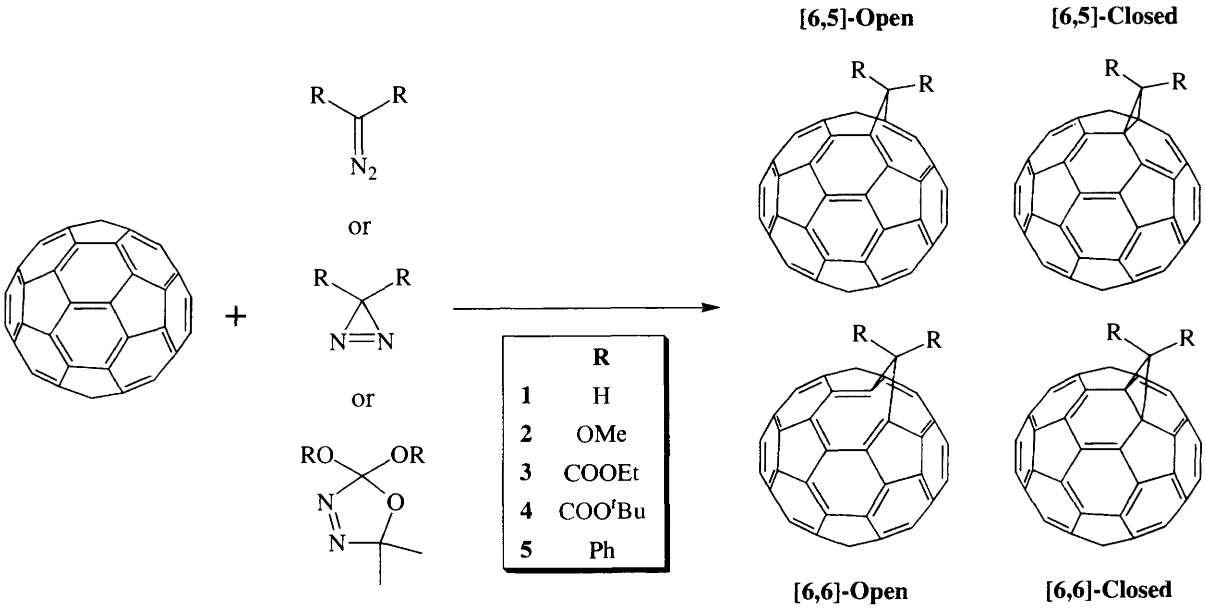
Valence Isomerism and Rearrangements in Methanofullerenes

François Diederich,* Lyle Isaacs and Douglas Philp
Laboratorium für Organische Chemie, ETH Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

A PM3 computational and experimental study of the methanofullerenes **1**–**5** demonstrates that the electronic basis for the experimentally preferred formation of the [6,6]-closed and [6,5]-open over the [6,6]-open and [6,5]-closed isomers of methanofullerenes is the preservation of the [5]radialene-type bonding pattern found in C_{60} by these two structures. The [6,5]-open is the less stable of the two experimentally isolated isomers as a result of the violation of Bredt's Rule. The PM3 method locates a [6,5]-closed structure for the methanofullerenes **2**–**5**, but not for **1**. This suggests that the thermal interconversion of the [6,5]-open and [6,6]-closed isomers can only occur *via* a stepwise mechanism—[6,5]-open to [6,5]-closed valence isomerisation followed by a 1,5-shift—in cases where the corresponding [6,5]-closed structure is located in a local energy minimum.

The interesting physical properties[1] of C_{60} have encouraged chemists to design and synthesise functional derivatives[2,3] which may possess desirable properties. Among the established functionalisation methods, the addition of diazo compounds[4,5] (Fig. 1) has attracted particular attention as a result of the interesting electronic structures, which largely preserve the C_{60} chromophore, of the methanofullerenes produced. It has been shown that, of the four possible products of the addition reaction, the kinetic products[6–8] are those possessing a [6,5]-open geometry (Fig. 1). Thermal rearrangement[7–10] of the kinetic products affords the thermodynamically more stable [6,6]-closed isomers (Fig. 1). ^{13}C NMR spectroscopy has resolved[5,7,11] the initial debate over the valence isomeric preferences of the methanofullerenes, and a simple valence bond rationale has been proposed[8,10] to explain these preferences. According to this model, the [6,6]-closed and [6,5]-open structures are preferred since the double bonds in these valence isomers maintain the [5]radialene-type pattern of bonding observed in C_{60}, *i.e.*, the double bonds are located at the [6,6]-ring junctions.[12] Here, we present a comprehensive computational study of experimentally accessible methanofullerenes. We demonstrate (*i*) the electronic structural basis for the observed valence isomeric preferences across a wide range of substituents at the bridging carbon centre, and (*ii*) apply these results in the elucidation of a feasible pathway for the thermal rearrangement reaction.

The heats of formation and minimum-energy structures of the two experimentally observed isomers—namely the [6,5]-open and the [6,6]-closed—were calculated using the PM3 method[13,]† for the methanofullerenes **1**–**5**. The calculated relative heats of formation of these compounds are shown in Table 1. For the methanofullerenes **2**–**5** (R = OMe, COOEt, COOBu^t, Ph), the [6,6]-closed isomer is predicted to be



	R
1	H
2	OMe
3	COOEt
4	COO^{t}Bu
5	Ph

Fig. 1 The four possible isomers arising from the addition of diazo compounds to C_{60}

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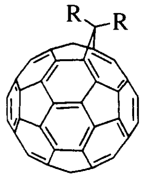
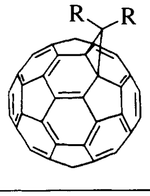
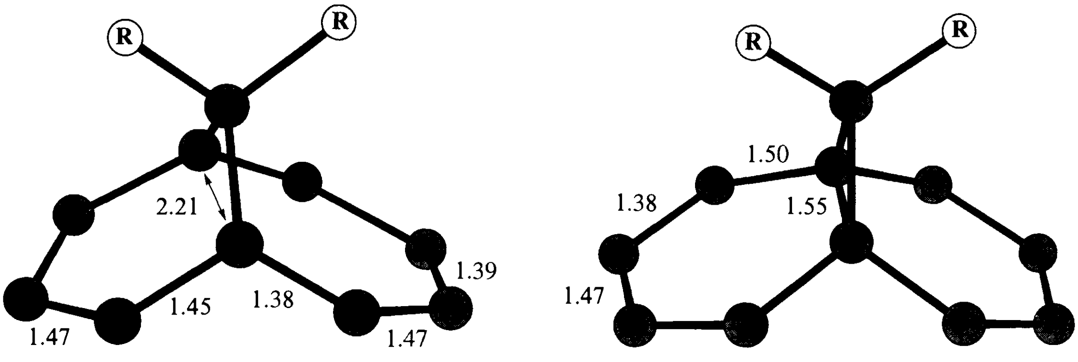
† We have also carried out these calculations using the AM1 method (M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902) for comparison purposes. Surprisingly, the results obtained using AM1 were found to deviate significantly from those expected from experimental data—AM1 consistently predicts the [6,5]-open isomer to be more stable than the [6,6]-closed isomer. Wudl and co-workers have reported[8] that the older MNDO method (M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899) successfully predicts the [6,6]-closed isomer to be more stable than the [6,5]-open isomer, although no relative heats of formation are given.

Table 1 Calculated relative heats of formation[a] for methanofullerene derivatives 1–5

		1	2	3	4	5
	[6,5]-Open	0	+4.70	+6.06	+6.26	+7.31
	[6,6]-Closed	+0.34	0	0	0	0

[a] Calculated using the PM3 Hamiltonian.[13] Values are in kcal mol^{-1} relative to the most stable isomer for each compound.



(a) (b)

Fig. 2 Calculated PM3 mean geometries for (a) the [6,5]-open and (b) [6,6]-closed isomers of methanofullerenes 1–5. Quoted bond lengths (Å) are the mean values taken over all five compounds. Variations in bond lengths across the series 1–5 are ±0.01 Å, respectively. The remainder of the fullerene sphere has been removed for clarity in each case.

significantly more stable than the [6,5]-open isomer. In the case of 1, however, PM3 predicts the two isomers to be almost equal in energy. This observation is at variance with the results reported by Raghavachari and Sosa[14] who predict, on the basis of high-level *ab initio* calculations, the [6,6]-closed isomer to be more stable by 2.5 kcal mol^{-1}. It should be noted, however, that the energy difference calculated here (0.34 kcal mol^{-1} in favour of the [6,5]-open isomer) is more consistent with the isomer distribution observed[15] for 1 prepared by photolysis of the 1-pyrazoline formed by addition of CH_2N_2 to C_{60}. Examination of the calculated structures for both the [6,5]-open and [6,6]-closed isomers of 1–5 reveals a remarkable invariance in the geometries (Fig. 2) of the 1,5- and 1,6-methanoannulene sub-units within the fullerene spheres of 1–5. Despite the widely differing electronic properties of the substituents on the bridging carbon atom in 1–5, the calculated transannular distances and bond lengths all lie within ±0.01 Å of the mean values for the five compounds studied. Thus, the calculated transannular distances are 2.21 ± 0.01 Å for the [6,5]-open isomers of 1–5 and 1.55 ± 0.01 Å for the corresponding [6,6]-closed isomers. The lack of variation in the calculated geometries suggests strongly that the position of the valence isomeric equilibrium is decided, not by the electronic properties of the bridging substituents, but rather by the rigidity and electronic structure of the fullerene sphere itself.

The reaction coordinate for the opening of the transannular bond in the [6,6]-closed isomer of 1 has been reported at the MNDO and HF/3-21G levels by Raghavachari and Sosa.[14] We have repeated this calculation using the PM3 method [Fig. 3(*a*)] and, in addition, investigated the same reaction coordinate for 2–5 [Fig. 3(*a*)]. The opening of the [6,6]-transannular bond is found to be a relatively low-energy process, although the energy increases rapidly at transannular distances greater than 2.20 Å. In agreement with the results presented by Raghavachari and Sosa,[14] there is no minimum observed in any case which corresponds to a [6,6]-open structure. We have also investigated the reaction coordinate for the closing of the transannular gap in the [6,5]-open isomer [Fig. 3(*b*)] at the PM3 level. In this case, the ring closure process is more costly in terms of energy. In addition, in the cases of 2–5, we located a new, shallow minimum* corresponding to a [6,5]-closed structure. The mean geometries and relative energies of the [6,5]-closed isomers of 2–5 are summarised in Fig. 4. Again the calculated geometries do not vary across the series of substituents studied, once more implying that substituent effects arising from the bridging carbon atom are absent in methanofullerenes. The most notable feature of the [6,5]-closed structure is the long transannular bond, which, at

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* Although Wudl and co-workers have noted the observation of other products from the addition of diazo compounds to C_{60} (see comments in F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157), it is unlikely that any of these corresponds to the [6,5]-closed isomer. The enthalpy of activation for the conversion of this isomer into the more stable [6,5]-open isomer is calculated to be < 1 kcal mol^{-1}.

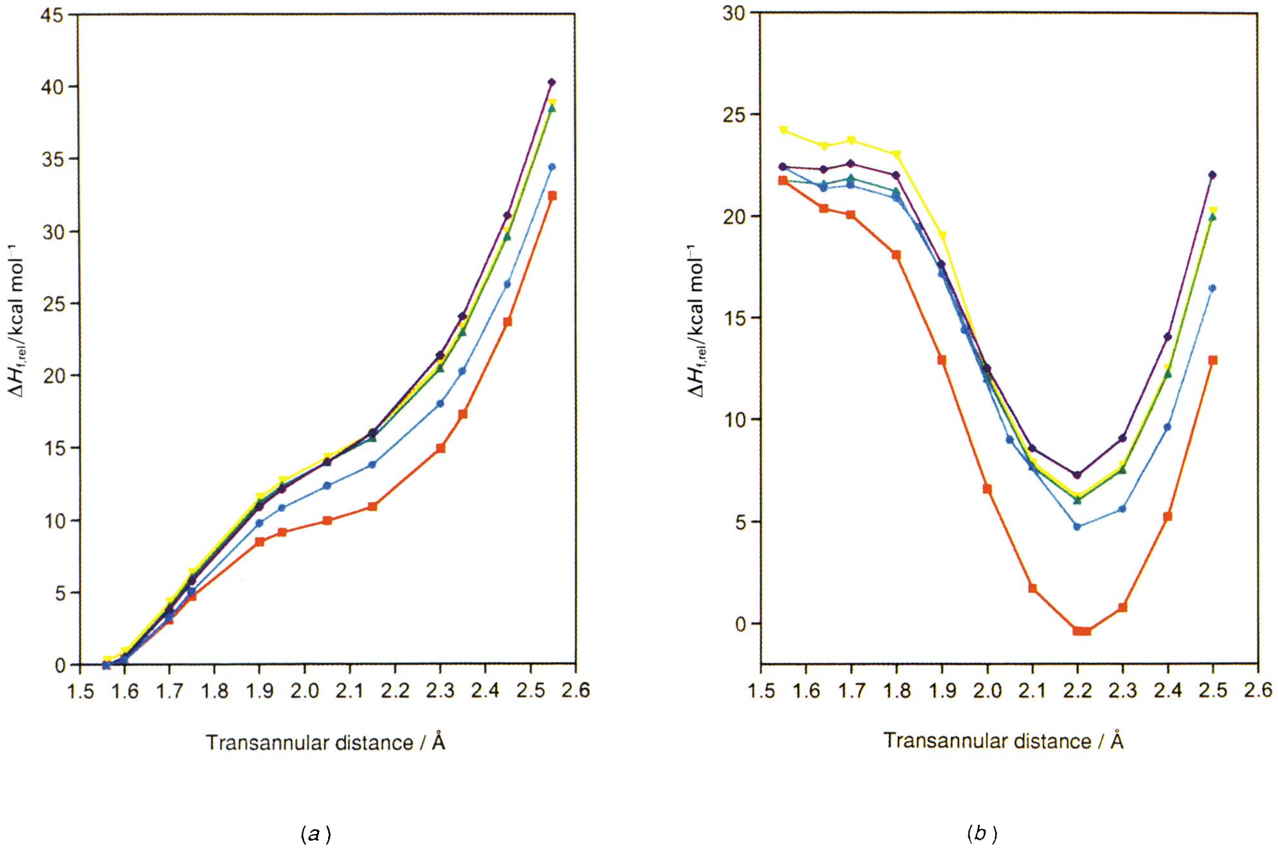
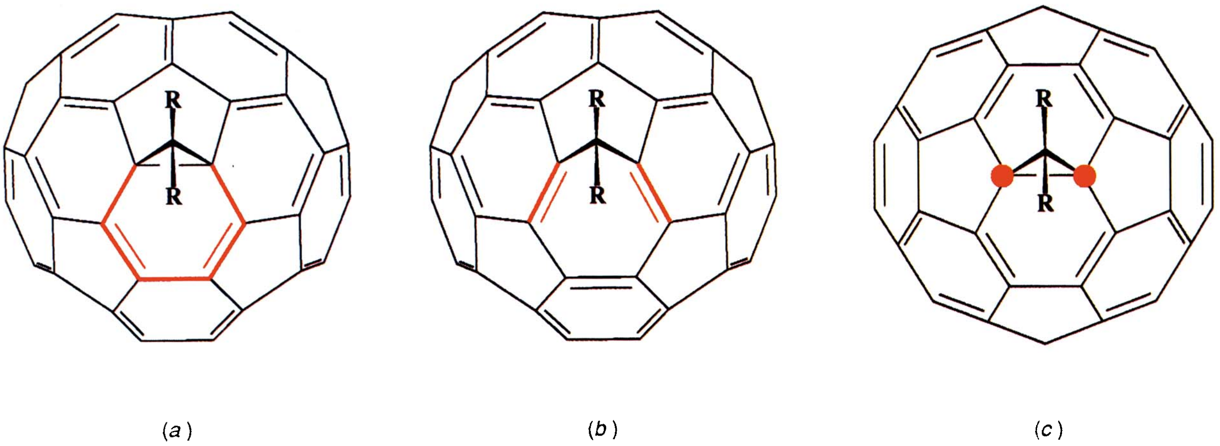


Fig. 3 Minimum-energy reaction pathways calculated using PM3 for (*a*) the opening of the [6,6]-closed transannular bond and (*b*) the closing of the [6,5]-open transannular gap. The curves are plotted relative to the heat of formation of the [6,6]-closed isomer in each case. The curves are colour coded as follows: red, **1**; blue, **2**; green, **3**; yellow, **4**; magenta, **5**.



(a) (b) (c)

Fig. 5 Trends in stability: (*a*) localisation of unfavourable double bonds in the [6,5]-closed structure; (*b*) Bredt's rule violation in the [6,5]-open structure; (*c*) sp^3-hybridised centres at the bridgeheads in the [6,6]-closed structure. The bonding depicted in these structures is derived from bond-order analyses of the calculated structures for **1**–**5**.

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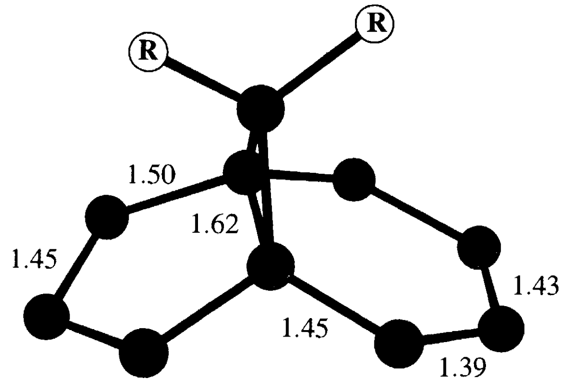


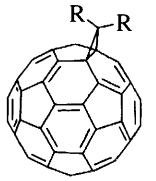
	1	2	3	4	5
 [6,5]-Closed	NM	+21.40	+21.72	+21.75	+21.69

Fig. 4 Calculated structures and relative heats of formation (RHOF) for the [6,5]-closed isomers of methanofullerenes **2**–**5**. Structures and RHOFs were calculated using the PM3 method. RHOF values are in kcal mol^{-1} relative to the [6,6]-closed isomer for each compound. NM = no minimum located corresponding to this structure. Conventions used in quoting geometries are the same as those in Fig. 2. The remainder of the fullerene sphere has been removed for clarity.

1.62 ± 0.01 Å, is some 0.07 Å longer than the corresponding bond in the [6,6]-closed isomer.

Closer examination of the calculated geometries and bond orders[16] within the three isomers of the methanofullerenes **1**–**5** reveals the electronic basis for the observed trend in relative stabilities. We note [Fig. 5(*a*)] that the (6,5)-closed isomer is forced to locate two formal double bonds within five-membered rings of the fullerene sphere, disrupting the favourable [5]radialene-type structure preferred[12] by C_{60}. The [6,5]-open isomer [Fig. 5(*b*)] can avoid placing formal double bonds within five-membered rings, but can only achieve this at the expense of placing formal double bonds at the bridgehead carbon atoms, in violation of Bredt's Rule. Evidence for this strain can be found in the geometry of the formally sp^2-hybridised bridgehead carbon atoms—these are pulled out of the plane of the three adjacent carbon atoms by 0.22 ± 0.02 Å. The [6,6]-closed isomer [Fig. 5(*c*)] is the most stable as it can avoid placing formal double bonds in five-membered rings and violation of Bredt's Rule by creating sp^3-hybridised bridgehead carbon atoms, which, although located in a three-membered ring, cannot be regarded as particularly unfavourable.*

Experimentally, it has proved possible to rearrange the [6,5]-open isomers of both the malonyl ester derivatives† **3** and **4**, and the diphenyl compound **5** to the [6,6]-closed isomers. Smith *et al.* have reported[15] that the [6,6]-closed isomer of the parent methanofullerene **1** cannot be thermally rearranged to the corresponding [6,5]-open isomer. We have determined independently (see the Experimental section) that the [6,5]-open isomer cannot be rearranged to the [6,6]-closed isomer. Only when these two observations are taken together can the existence of a thermally accessible rearrangement pathway for the interconversion of the isomers of **1** be completely ruled out. The location of a local minimum corresponding to the [6,5]-closed structure in the cases of **2**–**5**, but *not* for **1**, intrigued us. Two pathways for the rearrangement can be envisaged. The first involves the electrocyclic closure of the [6,5]-transannular bond, followed by a thermally allowed [1,5]-sigmatropic shift of the bridging carbon from the [6,5]- to the [6,6]-ring junction. The second possibility involves concerted ring closure and migration steps. The experimental results can be explained satisfactorily if we invoke the stepwise mechanism, passing through the [6,5]-closed structure, for the rearrangement process. Thus, the absence of an energy minimum representing the [6,5]-closed isomer in the case of **1** would preclude the thermal rearrangement of this compound. However, the location of a [6,5]-closed structure in a shallow energy minimum in the cases of **2**–**5** would permit thermal rearrangement *via* the stepwise pathway.

The results of this study clearly demonstrate that the electronic basis for the experimentally preferred formation of the [6,6]-closed and [6,5]-open methanofullerenes is the preservation of the bonding pattern within C_{60} by these two structures. The relative stability of these two isomers reflects the degree to which their electronic structure matches that of C_{60}. The location of a [6,5]-closed structure for the methanofullerenes **2**–**5**, which have been shown to rearrange thermally, and the absence of a similar structure for **1**, where thermal rearrangement is not observed experimentally,‡ suggest that the thermal interconversion of the [6,5]-open and [6,6]-closed isomers can only occur in cases where the corresponding [6,5]-closed structure is located in a local energy minimum, *i.e.*, *via* a stepwise mechanism. In conclusion, this study demonstrates the utility of semiempirical molecular orbital methods as a predictive tool§ in the chemistry of methanofullerenes.

Experimental

Diethyl 1,2-*Dihydro*-1,2-*methanofullerene*[60]-61,61-*dicarboxylate* **3**.—A mixture of C_{60} (200 mg, 0.28 mmol) and diethyl diazomalonate (517 mg, 2.8 mmol) was dissolved in toluene (100 cm^3) and heated at reflux for 20 h. The red solution was adsorbed onto silica gel (40 g) and chromatographed, eluting first with toluene–hexane (1 : 1), to remove residual C_{60}, and then with pure toluene to elute the methanofullerenes as an isomeric mixture, as determined by ^1H NMR analysis. The isomeric mixture was dissolved in chlorobenzene (100 cm^3) and heated at reflux for 24 h. Chromatography [SiO_2; toluene–hexane (1 : 1), then pure toluene], recrystallisation from $CHCl_3$–MeOH, and drying (0.1 torr, 60 °C, 6 h) afforded **3** as a dark solid (25 mg, 10%). M.p. > 270 °C. δ_H(200 MHz; $CDCl_3$) 4.57

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* Extending this analysis, it is not surprising that the [6,6]-open isomer does not correspond to a stable structure. It not only incorporates *three* double bonds within five-membered rings, destroying the preferred [5]radialene-type bonding pattern of C_{60}, but also *two* of these double bonds occur at the bridgehead, thus, in addition, violating Bredt's Rule.

† Compound **3** has been synthesised independently by the treatment of C_{60} with bromodiethyl malonate under strongly basic conditions by Bingel (see, C. Bingel, *Chem. Ber.*, 1993, **126**, 1957).

‡ Nakamura and co-workers have performed AM1 and PM3 calculations on **1** (H. Tokuyama, M. Nakamura and E. Nakamura, *Tetrahedron Lett.*, 1993, **34**, 7429) and have attempted to use these results to explain the thermal stability of their [6,6]-closed vinylcarbene adduct. Their choice of model compound is unfortunate, since we have demonstrated conclusively here that the parent methanofullerene **1** is *atypical* of the series we have studied, and that the [6,6]-closed isomer can be expected to be considerably more stable than the corresponding [6,5]-open isomer in most cases.

§ Interestingly, the results presented here for the methanofullerenes are also consistent with the experimental results obtained for the annellation of larger rings to C_{60}. Of the two low-energy structures, the [6,5]-open geometry is incompatible with the presence of four, five and six membered rings as a result of the severe angle deformation required at the formally sp^2-hybridised bridgehead carbon atoms. It is therefore unsurprising that only [6,6]-closed structures have been observed in these cases.

(4 H, q, J = 7 Hz) and 1.53 (6 H, t, J = 7 Hz); δ_C(125 MHz; $CDCl_3$) 163.61, 145.33, 145.27, 145.20, 145.19, 144.89, 144.70, 144.68, 144.62, 143.89, 143.09, 143.02, 143.00, 142.22, 141.93, 140.95, 139.04, 71.61, 63.42, 52.21 and 14.25; m/z (FABMS) 879 ([M + 1]$^+$).

Di-tert-*butyl* 1,2-*Dihydro*-1,2-*methanofullerene*[60]-61,61-*dicarboxylate* **4**.—A mixture of C_{60} (200 mg, 0.28 mmol) and di-*tert*-butyl diazomalonate (672 mg, 2.8 mmol) was dissolved in toluene (100 cm^3) and heated at reflux for 20 h. The red solution was adsorbed onto silica gel (40 g) and chromatographed, eluting first with toluene–hexane (1 : 1), to remove residual C_{60}, and then with pure toluene to elute the methanofullerenes as an isomeric mixture, as determined by ^1H NMR analysis. The isomeric mixture was dissolved in chlorobenzene (100 cm^3) and heated at reflux for 24 h. Chromatography [SiO_2; toluene–hexane (1 : 1), then pure toluene], recrystallisation from $CHCl_3$–MeOH, and drying (0.1 torr, 60 °C, 6 h) afforded **4** as a dark solid (18 mg, 7%). M.p. >270 °C; ν_{max}/cm^{-1} 2972w, 2922w, 2850w, 1740s, 1454w, 1427w, 1384w, 1367m, 1272m, 1250s, 1156s, 1113m, 578w and 526s; δ_H(300 MHz; $CDCl_3$) 1.70 (18 H, s); δ_C(125 MHz; $CDCl_3$) 162.48, 145.71, 145.53, 145.18, 145.10, 144.75 (× 2), 144.64, 144.47, 143.84, 143.05, 142.96, 142.94, 142.20, 141.92, 140.85, 138.90, 84.71, 72.20, 54.11 and 28.11; m/z (FABMS) 935 ([M + 1]$^+$).

Attempted Isomerisation of **1**.—The parent methanofullerene **1** was prepared by the method of Wudl and co-workers.[6] $C_{61}H_2$ (**1**) (46 mg, 0.63 mmol) was dissolved in chlorobenzene and heated at reflux for 24 h. After cooling, the solvent was removed *in vacuo* and the residual solid analysed by ^1H NMR spectroscopy [300 MHz; CS_2–C_6D_6 (2 : 1)]. No change in the [6,5]-open : [6,6]-closed isomer ratio (97 : 3) was detected.

Computational Studies.—Calculations were carried out on Silicon Graphics Personal Iris 4D/35TG, Indigo or Crimson workstations. Initial input structures were generated and minimised (CVFF forcefield) using the INSIGHT II/DISCOVER package (Version 2.2.0, Biosym Technologies Inc., San Diego, 1993). Semiempirical SCF-MO calculations were then performed using the MOPAC 6.0 program (*QCPE* 455). Geometry optimisations of the [6,5]-open and [6,6]-closed isomers were carried out on input structures using either the Broydon–Fletcher–Goldfarb–Shanno (BFGS) or the Eigenvector Following (EF) minimisation methods. All internal coordinates were optimised and gradient norms of less than 0.20 were achieved in all cases. All optimisations were performed in Cartesian coordinates. The structures obtained were characterised as local minima by means of a vibrational analysis (FORCE calculation). The reaction coordinates for the closing or opening of the transannular bond at the [6,5]- and [6,6]-ring junctions were calculated by driving the transannular distance in the molecular **Z**-matrix; all other internal coordinates were optimised. These calculations were performed using the EF method. Minimum-energy structures for the [6,5]-closed isomers of **2**–**5** were obtained from SCF-MO calculations, as described above for the other isomers, using starting structures obtained from the reaction coordinate calculations.

Acknowledgements

We thank the Royal Society for the award of a European Science Exchange Programme Fellowship (to D. P.) and the Swiss National Science Foundation for support of this work.

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Paper 3/07293B
Received 9*th December* 1993
Accepted 24*th December* 1993