Structures and energetics of dimeric fullerene and fullerene oxide derivatives

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Semi-empirical models confirm the stability of bridged dimer structures assigned in the literature to C_{120}, $C_{120}O$ and $C_{120}O_2$, interpreting all three as additions across formal double bonds of the C_{60} monomers. Analogous structures are proposed and compared for C_{60}/C_{70} dimers C_{130}, $C_{130}O$, $C_{130}O_2$, C_{140}, $C_{140}O$ and $C_{140}O_2$.

Introduction

With the preparation and characterisation of $C_{120}O_2$, a sequence of dimeric [60]fullerene derivatives has become available for study: the cycloadduct[1,2] $(C_{60})_2$, the furan-bridged[3] $(C_{60})_2O$ and the bis-furanoid[4] $(C_{60})_2O_2$. In the present paper we use qualitative molecular orbital calculations to explore structural similarities between these molecules and to predict structures for the homologous [60]/[70] and [70]/[70] species. Apparent differences between the bridging patterns, *e.g.* the fact that a four-membered ring links two hexagon–hexagon bonds in the proposed [2 + 2] structure of the [60]fullerene dimer[1] but two pentagon–hexagon bonds[4] in $(C_{60})_2O_2$, will be reconciled by a simple chemical argument supported by calculated relative energies of alternative structures.

Method

Calculations were carried out initially on families of isomeric dimers $(C_{60})_2O_n$ ($n = 0, 1, 2$) using the MNDO semi-empirical method[5] to optimise geometries, cross checked in several cases against other parameterisations (AM1 and PM3) and for all the most stable isomers against the independently derived density-functional tight-binding (DFTB) model.[6] Starting coordinates were obtained using molecular mechanics pre-optimisation, and no symmetry constraints were applied. As usual in working with semi-empirical methods, it is wise to trust only those trends that are reproduced by several models; it turns out here that all the methods used are agreed on the identities of the best isomeric forms, though not always on the order of the energies of their less stable competitors.

$C_{120}O_2$ has a ^{13}C NMR spectrum consistent with a dimeric structure in which hexagons of two [60]fullerene footballs are linked face-to-face by a (1,1′), (4,4′) pair of oxygen bridges and a (2,2′), (3,3′) pair of carbon–carbon bonds.[4] Although the structural assignment is not itself in doubt, it is useful to consider a wider family of isomeric structures in order to establish the degree of energetic preference for the observed isomer and to formulate predictive rules that may be used for homologues.

Calculations were therefore carried out on the ten structural isomers of the bridged dimer consistent with pairing *any* two connected chains of four sp^3 atoms by intermolecular bonds in the sequence C–O–C, C–C, C–C, C–O–C. The two furanoid rings are thus allowed to be either *cis* or *trans* to one another across a bridging four-membered ring, and the central four-membered ring itself may involve two hexagon–hexagon edges (*h*), two pentagon–hexagon edges (*p*), or one of each type. The isomers given by this recipe are illustrated in Fig. 1; of these, only $C_{120}O_2$: **1**, **6** and **7** would give rise to 32-line ^{13}C NMR spectra: their 4 × 2, 28 × 4 intensity patterns are all compatible with the recorded spectrum if the latter is assumed to include three 4 + 4 coincidences.[4]

In a similar spirit, the four isomers of $C_{120}O$ containing adjacent C–C and C–O–C bridges, and the four isomers of C_{120} containing adjacent C–C bridges (Fig. 1) were considered. Again, only isomer **1** of $C_{120}O$ is compatible with the observed 32-line ^{13}C NMR spectrum.[3] Theoretical predictions for the Raman and IR signatures of this isomer have been discussed and compared with the experimental data.[7]

Results†

The results of the calculations on $C_{120}O_n$ are summarised in Table 1. Within the chosen sets, the experimentally assigned structures for the dimers[1–4] are exactly those predicted to be of lowest total energy by both MNDO and DFTB models. For $C_{120}O_2$ this is isomer **6**, for $C_{120}O$ it is isomer **1**. It has already been shown by DFTB calculations that topologically different structures of $C_{120}O$, such as the epoxide form, are energetically much less favoured.[8] For C_{120} measured[9] and calculated[8] Raman spectra agree with the present and previous calculations on dimeric species[10–14] in favouring isomer C_{120} : **1**.

The pattern of energies of the less favoured isomers is also revealing in that there is an approximately linear penalty function associated with choice of the ‘wrong’ bond for formation of a bridging ring: in C_{120} the energies rise in the order $h/h < h/p < p/p$, with an increment of *ca.* 80 kJ mol^{-1} for each pentagonal edge that participates in the square ring; in $C_{120}O$ the penalty is slightly smaller, *ca.* 70 kJ mol^{-1} for each pentagonal edge of a furanoid ring. For $C_{120}O_2$, the best structures are those in which the whole chain of sp^3 atoms of each monomer is drawn from a single hexagonal face, thus forming a *cis* arrangement. Isomers of this type (**6**, **3**, **1**) are favoured by *ca.* 80 kJ mol^{-1} or more over the others. Within the favoured set, there is a small energetic preference of < *ca.* 20 kJ mol^{-1} per *h*

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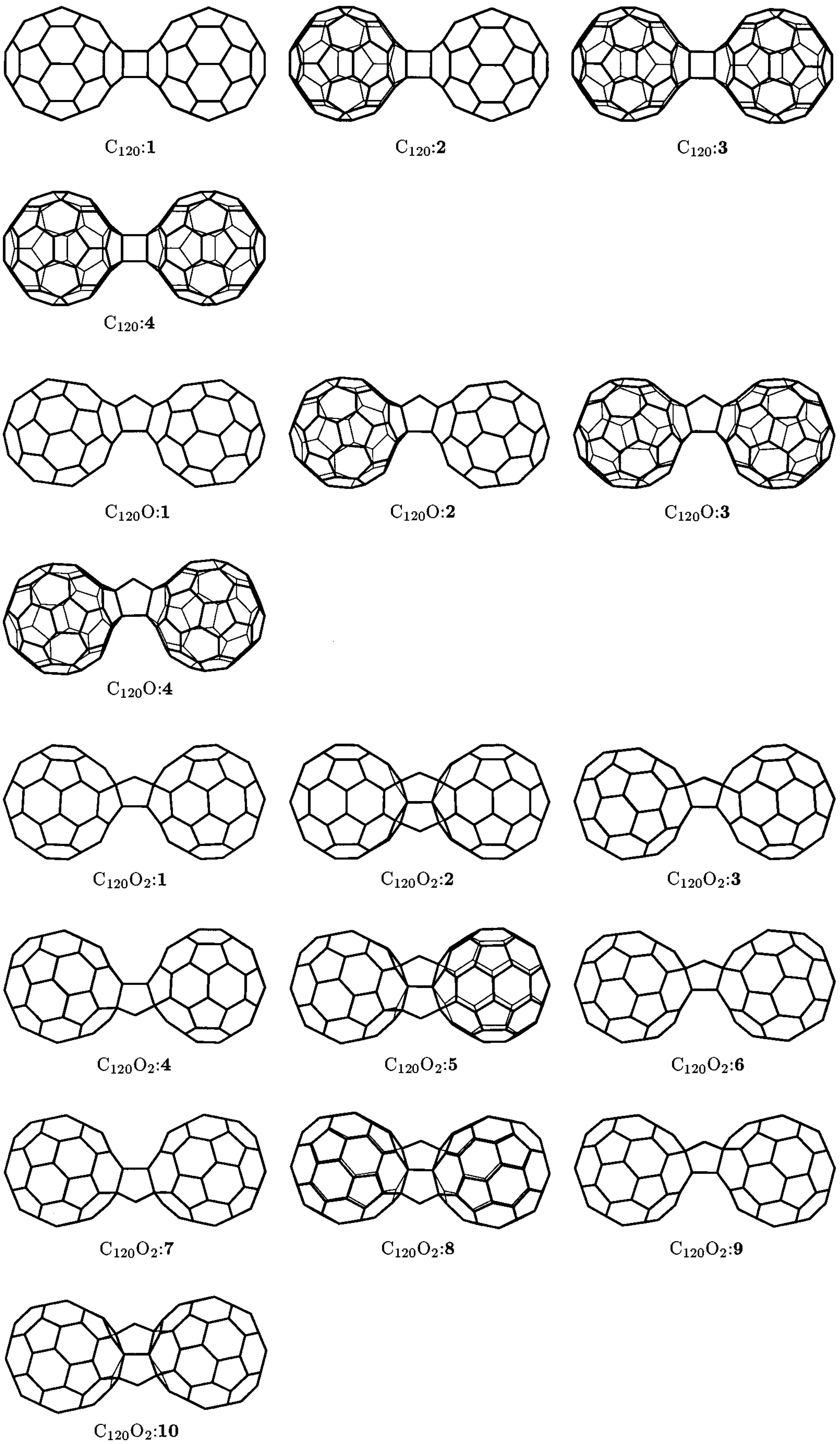
† *Note added in proof:* With the solid-state synthesis of a C_{60} dimer (G. W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583) a ^{13}C NMR spectrum and X-ray structural determination are now available and are consistent with isomer C_{120} : **1**. The X-ray bond lengths of the bridging four-membered ring are almost equal [*inter* 1.575(7) Å, *intra* 1.581(7) Å], in contrast with the rectangular MNDO structure (1.561 Å, 1.616 Å) but in closer agreement with the DFTB calculations reported here (1.585 Å, 1.595 Å).



C_{120}:**1** C_{120}:**2** C_{120}:**3**

C_{120}:**4**

$C_{120}O$:**1** $C_{120}O$:**2** $C_{120}O$:**3**

$C_{120}O$:**4**

$C_{120}O_2$:**1** $C_{120}O_2$:**2** $C_{120}O_2$:**3**

$C_{120}O_2$:**4** $C_{120}O_2$:**5** $C_{120}O_2$:**6**

$C_{120}O_2$:**7** $C_{120}O_2$:**8** $C_{120}O_2$:**9**

$C_{120}O_2$:**10**

Fig. 1 Optimised structures (at the MNDO level) for the candidate set of bridged isomers of C_{120}, $C_{120}O$ and $C_{120}O_2$. Isomers **2**, **5**, **8** and **10** of $C_{120}O_2$ have a *trans* pair of furanoid bridging rings, whereas isomers $C_{120}O_2$: **1**, **3**, **4**, **6**, **7** and **9** have the *cis*, basket-like arrangement at the bridge.

edge involved in a furanoid ring. The calculated energy penalties are consistent between the different semi-empirical methods (with, for example, the $C_{120}O_2$ preference for *h* edges rising from 15 to 19 and 20 kJ mol^{-1} in MNDO, PM3 and AM1 models, respectively) and they suggest a simple rationalisation of the preferred structures.

Although C_{60} has 12 500 Kekulé structures,[15] its addition chemistry, in which it behaves as an electron-deficient alkene,[16] and the marked bond alternation in its geometric structure[17] point to the dominance of just one of these: that in which all *p* edges are formal single bonds and all *h* edges are formally double. Formation of a dimer bridged by a single ring will thus be most favoured when it is an addition across a formal double bond, leaving the rest of the dominant Kekulé structure undisturbed. Utilisation of a pentagon edge in the bridging ring will force double bond character into pentagons elsewhere on the C_{60} ball, with a consequent energetic penalty. For dimers bridged by two rings, this electronic requirement can be fully satisfied only in a *cis* arrangement, which has the additional advantage of meeting the geometrical requirements of each bridging ring with minimal distortion of the monomers (compare *e.g.* $C_{120}O_2$: **6** and **8** in Fig. 1). The local structure around the bridge in $C_{120}O_2$: **6** can be seen in more detail in Fig. 2.

A different structure for $C_{120}O_2$ was also considered, in which the bridge was a single dioxinoid ring linking *h*/*h* monomer edges. The bridge is forced into an unfavourable non-planar configuration, and the structure lies higher in energy than the best seven bis-furanoid isomers, supporting the choice of the latter in the explanation of the experimental observations.

All three dimeric structures C_{120} : **1**, $C_{120}O$: **1** and $C_{120}O_2$: **6** are predicted to be bound with respect to the monomers, according to the MNDO model. The calculated energy differences $(C_{60})_2 - 2(C_{60})$, $(C_{60})_2O - C_{60}O - C_{60}$, and $(C_{60})_2O_2 - 2(C_{60}O)$, where C_{60} and $C_{60}O$ denote fullerene and best epoxide structures optimised at the same level of theory as the dimer, are 205, 231 and 461 kJ mol^{-1}, respectively, in the MNDO approximation, and reflect the driving force of σ bond formation in this model. DFTB calculations give smaller binding energies, with 29, 198 and 296 kJ mol^{-1}, for the species with 0, 1 and 2 oxygen atoms in the bridge, respectively. The largest difference between methods is obtained for the C_{120} dimer, which is only just bound at the DFTB level. However, the rather small DFTB binding energy of C_{120} is in good agreement with the results of SCF-DFT calculations including gradient corrections for the exchange-correlation potential.[8] The relatively small energy gain for the dimerization of C_{60} is taken to indicate a steric strain in the square ring of the dimer that is not counter-

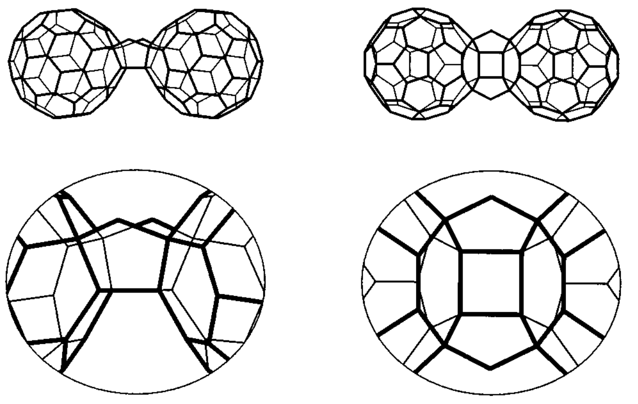


Fig. 2 Detail of the optimised structure of isomer **6** of $C_{120}O_2$, predicted to have the lowest energy in the set of candidates (see Table 1). Two approximately orthogonal views of the bridging portion of the structure are shown.

Table 1 Relative energies of isomeric C_{60} fullerene dimers and oxygenated dimers. Isomers, numbered *N*, are described by their point group *G*, sequence of bonds on each monomer involved in bridging, idealised ^{13}C NMR pattern of intensities, and relative energies as calculated in the MNDO (ΔE_M) and DFTB (ΔE_D) models, all in kJ mol^{-1}. *p* and *h* denote pentagon–hexagon and hexagon–hexagon edges of the C_{60} cage. Optimised structures for the isomers are illustrated in Fig. 1

Formula	*N*	*G*	Description	NMR signature	ΔE_M	ΔE_D
C_{120}	1	D_{2h}	*h*/*h*	4 × 4, 13 × 8	0.0	0.0
	2	C_s	*p*/*h*	8 × 1, 56 × 2	77.6	81.1
	3	C_{2v}	*p*/*p*	4 × 2, 28 × 4	156.3	162.9
	4	C_{2h}	*p*/*p*	4 × 2, 28 × 4	155.0	162.0
$C_{120}O$	1	C_{2v}	*h*/*h*	4 × 2, 28 × 4	0.0	0.0
	2	C_1	*p*/*h*	120 × 1	65.6	73.1
	3	C_s	*p*/*p*	60 × 2	131.7	145.4
	4	C_2	*p*/*p*	60 × 2	131.0	144.5
$C_{120}O_2$	1	C_{2v}	*p*,*h*,*p*/*p*,*h*,*p*	4 × 2, 28 × 4	57.9	76.2
	2	C_{2h}	*p*,*h*,*p*/*p*,*h*,*p*	30 × 4	450.6	262.0
	3	C_s	*h*,*p*,*h*/*p*,*h*,*p*	8 × 1, 56 × 2	29.0	38.3
	4	C_s	*p*,*p*,*p*/*p*,*h*,*p*	8 × 1, 56 × 2	227.8	233.1
	5	C_1	*h*,*p*,*p*/*p*,*h*,*p*	120 × 1	317.4	217.2
	6	C_{2v}	*h*,*p*,*h*/*h*,*p*,*h*	4 × 2, 28 × 4	0.0	0.0
	7	C_{2v}	*p*,*p*,*p*/*p*,*p*,*p*	4 × 2, 28 × 4	325.2	334.3
	8	C_s	*h*,*p*,*p*/*h*,*p*,*p*	60 × 2	145.2	153.3
	9	C_s	*h*,*p*,*h*/*p*,*p*,*p*	8 × 1, 56 × 2	200.5	195.6
	10	C_i	*h*,*p*,*p*/*p*,*p*,*h*	60 × 2	175.3	178.5

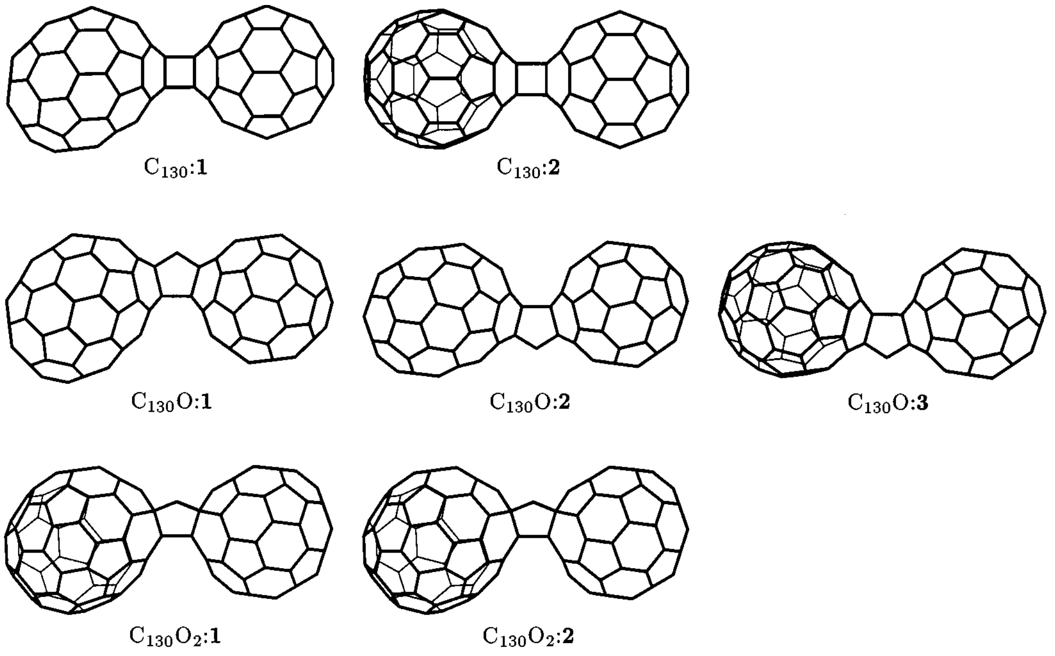
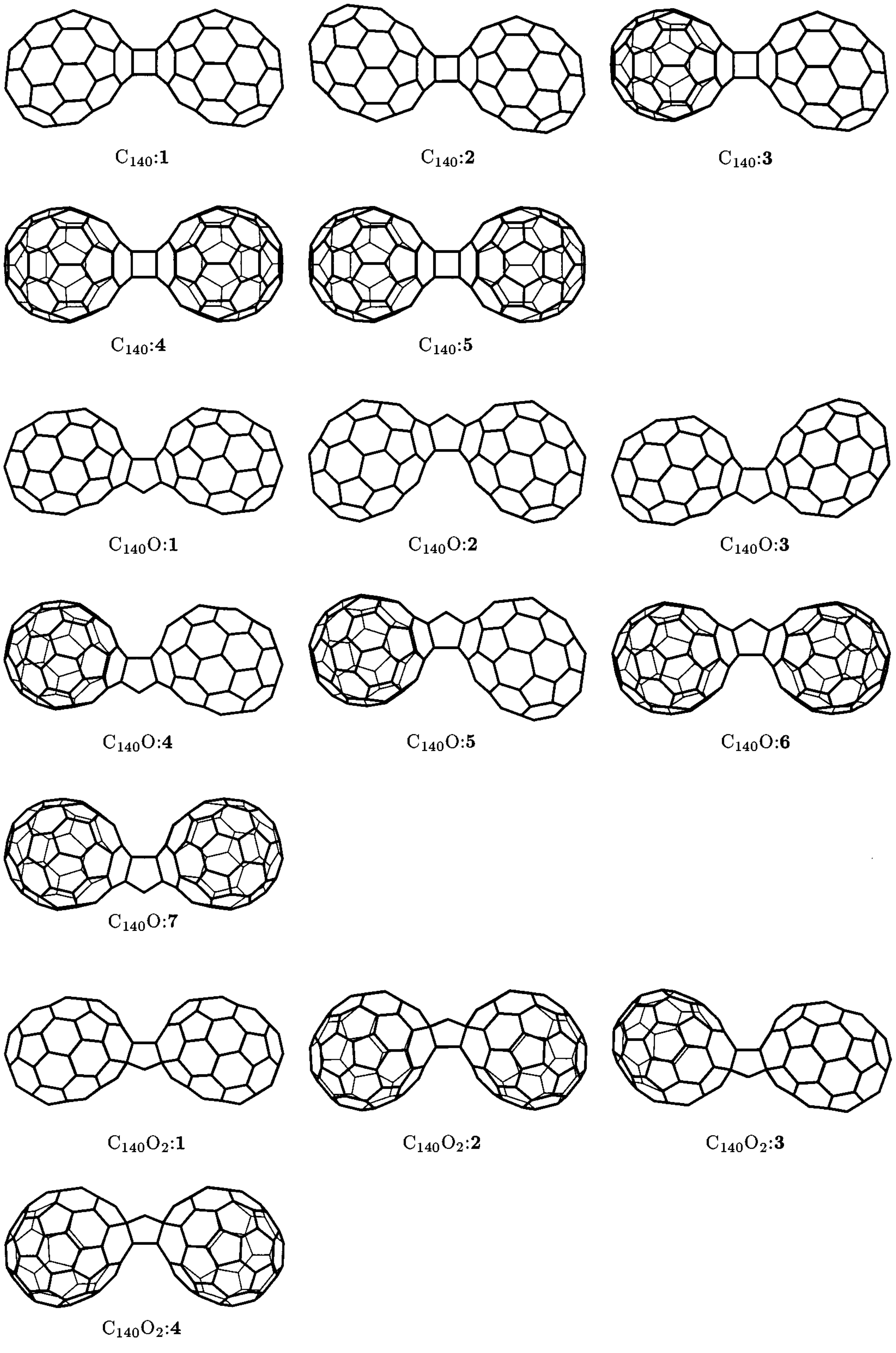


Fig. 3 Optimised structures (at the MNDO level) for the candidate set of bridged isomers of C_{130}, $C_{130}O$ and $C_{130}O_2$



C_{140}:**1** C_{140}:**2** C_{140}:**3**

C_{140}:**4** C_{140}:**5**

$C_{140}O$:**1** $C_{140}O$:**2** $C_{140}O$:**3**

$C_{140}O$:**4** $C_{140}O$:**5** $C_{140}O$:**6**

$C_{140}O$:**7**

$C_{140}O_2$:**1** $C_{140}O_2$:**2** $C_{140}O_2$:**3**

$C_{140}O_2$:**4**

Fig. 4 Optimised structures (at the MNDO level) for the candidate set of bridged isomers of C_{140}, $C_{140}O$ and $C_{140}O_2$

balanced as it is in the bis-furanoid $C_{120}O_2$ species by the formation of more σ-bonded rings.

The possibility of trimerisation and further oligomerisation has been discussed for the fullerenes[8,18] and fullerene oxides.[19]

Given the simplicity of the structure–energy relationship for C_{60} dimeric derivatives, it is tempting to extend the calculations to predict structures for C_{60}/C_{70} and C_{70}/C_{70} dimers. C_{70} behaves both magnetically[20,21] and chemically[22] as a composite of C_{60}-like hemispheres linked by an aromatic central belt, and formal double bonds are limited to its capping regions. It was therefore decided to construct isomers of C_{130}, $C_{130}O$, $C_{130}O_2$, C_{140}, $C_{140}O$ and $C_{140}O_2$ in which the bridging rings utilised only 'Stone–Wales'[23] formal double bonds *i.e.* those at the centre of pyracylene-like patches, belonging to two fused hexagons and joining atoms of two distinct pentagons. All 30 double bonds of C_{60}, but only 20 of the 105 edges of C_{70} are of this type. In each cap five 'polar' double bonds (*o*) radiate from the pentagon on the five-fold axis, and five 'tropical' (*t*) bonds below them link a circuit of five pentagons. Such bonds would be numbered (1,2) and (5,6), respectively, in the notation of ref. 24. The numbers of isomers compatible with attack on these formal double bonds are very limited, and it proved possible to obtain MNDO

Table 2 Relative energies of isomeric C_{60}/C_{70} fullerene dimers and oxygenated dimers. *o* and *t* denote 'polar' and 'tropical' Stone–Wales bonds of the C_{70} cage, as described in the text. For other notation and conventions see Table 1. Optimised structures for the isomers are illustrated in Fig. 3

Formula	*N*	*G*	Description	NMR signature	ΔE_M
C_{130}	1	C_s	*o/h*	8 × 1, 61 × 2	0.0
	2	C_s	*t/h*	8 × 1, 61 × 2	4.5
$C_{130}O$	1	C_s	*o/h*	8 × 1, 61 × 2	0.0
	2	C_s	*o/h*	8 × 1, 61 × 2	0.4
	3	C_1	*t/h*	120 × 1	3.6
$C_{130}O_2$	1	C_1	*o,p,t/h,p,h*	120 × 1	0.0
	2	C_s	*o,p,o/h,p,h*	8 × 1, 61 × 2	1.1

Table 3 Relative energies of isomeric C_{70} fullerene dimers and oxygenated dimers. Notation and conventions are as in Table 2. Optimised structures for the isomers are illustrated in Fig. 4

Formula	*N*	*G*	Description	NMR signature	ΔE_M
C_{140}	1	C_{2v}	*o/o*	4 × 2, 33 × 4	0.0
	2	C_{2h}	*o/o*	4 × 2, 33 × 4	0.0
	3	C_1	*o/t*	140 × 1	4.5
	4	C_{2v}	*t/t*	4 × 2, 33 × 4	9.2
	5	C_{2h}	*t/t*	4 × 2, 33 × 4	9.1
$C_{140}O$	1	C_{2v}	*o/o*	4 × 2, 33 × 4	0.8
	2	C_{2v}	*o/o*	4 × 2, 33 × 4	0.0
	3	C_s	*o/o*	8 × 1, 66 × 2	0.4
	4	C_1	*o/t*	140 × 1	3.9
	5	C_1	*o/t*	140 × 1	3.5
	6	C_s	*t/t*	70 × 2	7.2
	7	C_2	*t/t*	70 × 2	7.1
$C_{140}O_2$	1	C_{2v}	*o,p,o/o,p,o*	4 × 2, 33 × 4	2.2
	2	C_s	*o,p,t/o,p,t*	70 × 2	0.0
	3	C_1	*o,p,o/o,p,t*	140 × 1	1.1
	4	C_2	*o,p,t/t,p,o*	70 × 2	0.0

optimised geometries and energies for all of them (Figs. 3 and 4, Tables 2 and 3).

The significant feature of Tables 2 and 3 is that all isomeric structures constructed by addition across the formal double bonds of C_{70} are relatively stable. Binding energies calculated as before by comparison of MNDO monomer and dimer results show increments of 4, 4 and 5 kJ mol^{-1} for the best $C_{130}O_n$ species over C_{120}, $C_{120}O$ and $C_{120}O_2$, respectively. These increments are doubled for $C_{140}O_n$. We note that of the three $C_{70}O$ structures that do not undergo ring-expansion on optimisation in the MNDO model,[25] the best two are the polar and tropical epoxides identified on the basis of ^{13}C NMR evidence in ref. 22. The MNDO results for the $C_{130}O_n$ and $C_{140}O_n$ species show a small but consistent preference (*ca.* 4 kJ mol^{-1}) for participation of polar bonds in the bridging furanoid rings. Differences of this order could easily be reversed on changing the parameterisation. Departure from addition across formal double bonds, for example by using equatorial bonds of C_{70} in the furan ring for $C_{140}O$ or 'sub-tropical' edges of the equatorial hexagon belt in a pair of furanoid rings for $C_{140}O_2$, leads, however, to large increases in total energy (*ca.* 400 kJ mol^{-1} and *ca.* 165 kJ mol^{-1}, respectively).

It is not profitable to speculate which of the group of similar low-energy double-bond bridged isomers will be the best overall at some higher level of theory, and all may occur in future experimental products. It may also be the case that the factor deciding the favoured experimental isomers will be their compatibility with the orientation of neighbouring molecules in the crystal, rather than their absolute thermodynamic stability.[26]

Acknowledgements

The authors thank the EU Human Capital and Mobility Scheme for financial support through the HCM Network on Fullerene Formation, Stability and Photophysics.

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Paper 7/03836D
Received 2*nd June* 1997
Accepted 18*th June* 1997