Hydrolysis of Phosphonoformate Triesters: Rate Acceleration of a Millionfold in Nucleophilic Substitution at Phosphorus[1]

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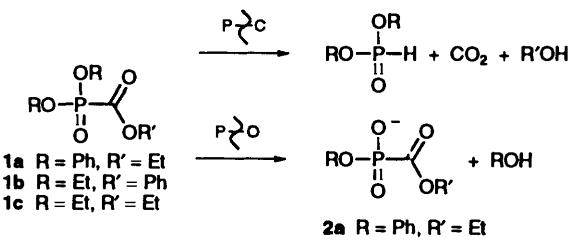
The base-catalysed hydrolysis of triesters of phosphonoformic acid *via* P–O bond cleavage proceeds at rates at least 10^4 times greater than diethyl difluoromethylphosphonate and 10^6 times greater than diphenyl methylphosphonate. Buffer catalysis and isotope labelling studies suggest the mechanism of rate acceleration by the ethoxycarbonyl group to involve either intramolecular nucleophilic catalyses *via* a three-membered ring or stereoelectronic assistance, both of which are unprecedented.

The reactivity of α-carbonyl phosphonates has been the subject of a number of studies,[2] the interest resting in the unusual lability of the P–C bond. Indeed, the lability of the P–C bond provides a major obstacle to the use of α-carbonyl phosphonates as therapeutic agents. Phosphonoformate (Foscavir, Foscarnet, PFA) is of clinical utility in AIDS therapy.[3] Several PFA triesters have been synthesized as prodrugs. Our initial communication highlighted the enhanced reactivity of these species, in particular towards P–C bond cleavage.[4] Subsequent work has confirmed the high reactivity of PFA triesters at neutral pH.[5] In dilute alkali solution we observed competitive P–O bond cleavage.[4] We now report that base-catalysed hydrolysis of diphenyl (ethoxycarbonyl)phosphonate (**1a**) occurs *via* exclusive P–O bond cleavage with a rate enhancement of 10^6. The mechanism of this rate acceleration is without precedent.

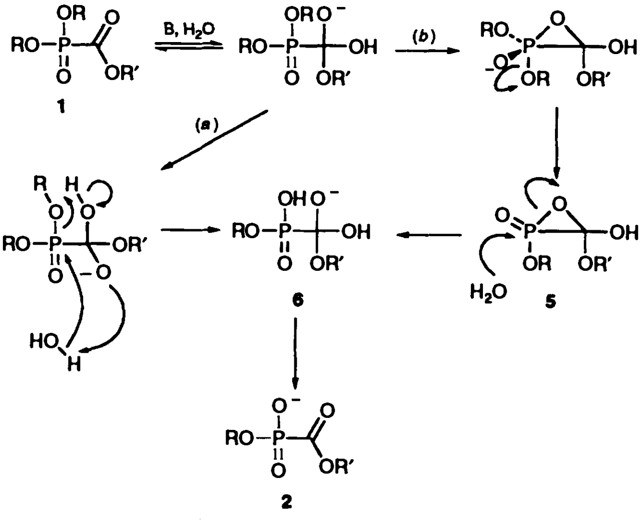
Initial attack at the carbon of PFA triesters leads to a tetrahedral intermediate which may break down by competitive P–C and C–O bond cleavage (Scheme 1). Attack at phosphorus results in P–O bond cleavage. *P*-alkoxy esters of PFA (*e.g.* **1b**) undergo base-catalysed hydrolysis *via* competitive P–C and P–O bond cleavage. The *P*-phenoxy ester **1a** undergoes base-catalysed hydrolysis by exclusive P–O bond cleavage at pH > 6.5, yielding the monoanion **2a** as product, although in 0.45 mol dm^{-3} NaOH further hydrolysis to PFA itself is observed. The rate of hydrolysis of **1a** at pH 7.0 is 10^6 times greater than that of diphenyl methylphosphonate (**3**) (Table 1).[6a] How does the alkoxycarbonyl group accelerate the rate of nucleophilic substitution at phosphorus?



Scheme 1 Initial Hydrolysis Products

The alkoxycarbonyl group is electron-withdrawing and as indicated by Taft parameters, this inductive effect should be similar to that of the CF_2H substituent.[7] The difference in base-catalysed rates for **1b** and diethyl difluoromethylphosphonate (**4**) is 10^4–10^5 (Table 1). This comparison is between PhOC(O) and CF_2H substituted esters—a better comparison is between the ethoxycarbonyl substituted ester **1c** and **3**. Hydrolysis of the triethyl ester **1c** at pH 9.5 is complete upon mixing and subsequent ^1H NMR measurement, giving 50% P–O bond cleavage,[4] whereas the half life for **4**, at this pH, corrected to room temperature, is *ca.* 100 h. It is clear that the electron-withdrawing effect of the carbon substituent in phosphonates **1a–c**, cannot alone account for the observed rates of nucleophilic substitution at phosphorus.† In addition, involvement of chelated metal ions is ruled out since rate shows no dependence on salt concentration.

Hydrolysis of alkoyl and aroyl phosphonates occurs by exclusive P–C bond cleavage *via* hydrate formation.[1] The hydrate formed from **1** has a pK_a estimated at 9.1.[8] Neighbouring group participation by the hydrate oxyanion may be envisaged by (i) bifunctional general acid–general base or (ii) intramolecular nucleophilic catalysis [Scheme 2, pathways (*a*) and (*b*) respectively].‡ The bifunctional process is ruled out by the observation of a substantial general base component in the buffer catalysis of hydrolysis of **1a** (Table 1). Hydrolysis of **1a**, at pH 9.5 in carbonate buffer, in the presence of ^{18}O-labelled water shows full label incorporation at the



Scheme 2

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† The study by Freeman's group of PFA trialkyl esters suggests a large rate acceleration and involves detailed product distribution and labelling studies, but the kinetic analysis does not allow for rigorous and exact determination of the rate enhancement nor mechanism. The rationale for rate enhacement is suggested to be the electron-withdrawing nature of the alkoxycarbonyl group.[5b]

‡ The nucleophilic catalysis pathway may be written by a number of routes involving general base-catalysed breakdown of the three-membered species and direct breakdown of the pentacoordinate species. Only the simplest route is shown.

Table 1 Second-order or pseudo-first-order rate constants calculated for hydrolysis of phosphonate esters in 60% aqueous MeCN

Ester	k_H· 10^{-3} dm^3 mol^{-1} s^{-1}	$k_0/10^{-5}$ s^{-1}	k_{OH^-} dm^3 mol^{-1} s^{-1}	k_B/dm^3 mol^{-1} s^{-1}
1a	—	—	2.56×10^{4} [a]	0.889 [b]
1a	—	—	6.29×10^{3} [c]	—
1b	4.5	140	2.55×10^{3} [a]	—
3	—	—	5.4×10^{-2} [d]	—
3	—	—	3.81 [e]	—
4	—	—	6.42×10^{-2} [f]	—

[a] At 36 °C. [b] At 17 °C. B = imidazole. [c] At 5 °C. [d] At 37 °C. Data for **1a. b** from monitoring of decay of substrate or formation of phenol product by UV–VIS spectroscopy. [d] At 40 °C. from ref. 6*a*. [e] At 100 °C in H_2O. from ref. 6*b*. [f] Data from pHstat method 8 < pH < 11.5 at 37 °C. All products confirmed by NMR spectroscopy and mass spec. analysis. Rate constants from fitting to $k(\text{obs}) = k_H\cdot[H^+] + k_0 + k_{OH^-}[OH^-]$. Salt effects found to be negligible. All reactions at pH > 6 in 0.1 mol dm^{-3} KCl.

phosphorus of **2** by ^{31}P NMR analysis, compatible with pathway (*b*). However, at pH 9.5, we observe only partial label incorporation at the acyl carbon of **2** by mass spectrometry.† The lack of full label incorporation at the acyl carbon requires that the hydrate oxygens do not become equivalent along the reaction pathway. If trapping of the initial hydrate oxyanion by the adjacent phosphorus is competitive with proton transfer and the hydrate **6** collapses before proton transfer. the labelling studies may be accommodated. However, (i) there is no precedent for formation of three-membered rings in rapid nucleophilic substitution at phosphorus.[9] and (ii) preliminary *ab initio* calculations at RHF/3-21 + G* suggest considerable strain in cyclic species such as **5**.‡ The geminal arrangement of reactive groups in the hydrate oxyanion is expected to accelerate the reaction. But, the dogma of associative nucleophilic substitution at phosphorus (*via* pentacoordinate trigonal bipyramidal intermediates or transition states)[10] would require re-examination to accommodate the highly distorted species that are entailed in this mechanism.

The effect of α-substituents on the rate of S_N2 reaction at carbon is well-documented.[11] Ethoxycarbonylchloromethane is reported to undergo substitution by iodide in acetone at a rate 6.8×10^2 times greater than ethyl chloride. The related reactivity effect of α-keto substituents has been explained by orbital interactions[12] and through Shaik's valence bond model.[13] It is possible that a similar, but hitherto unobserved, stereoelectronic effect is responsible for the enhanced reactivity of the triesters of PFA towards P–O bond cleavage. This mechanism would only permit label incorporation at acyl carbon *via* competitive and reversible hydrate formation. The large rate enhancement observed for nucleophilic substitution at phosphorus in this system demands a novel mechanism. Computational studies on PFA triesters and kinetic studies on hydrolysis of α-hydroxy phosphonates are in progress in order to distinguish between intramolecular nucleophilic catalysis and stereoelectronic assistance.

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† Freeman observes no label incorporation at pH 7.5 for hydrolysis of dibenzyl (methoxycarbonyl)phosphonate.[5]

‡ Full geometry optimization (HF/3-21 + G(*)//3-21 + G(*)) of HO_2-PCHO(OH) (a model for **5**) and H_2O_3PCHO (its acyclic analogue) yields a difference in energy of 35 kcal mol^{-1} in favour of the acylic species.

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The Tetravalence of C_{28}

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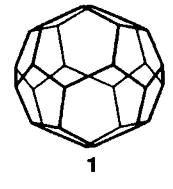
The tetravalence of tetrahedral C_{28} and the stabilities of the hypothetical species C_{28}^{4+}, $C_{28}H_4$ and U@C_{28} are all rationalised by a simple Hückel molecular orbital treatment that also predicts stability for $C_{24}N_4$.

Of the many possible isomers of C_{28}, just three[1] are compatible with the definition of a fullerene (a carbon cage with n vertices, $\frac{3}{2}n$ edges, 12 pentagonal and $\frac{1}{2}n - 10$ hexagonal faces). Two form an enantiomeric pair of structures with D_2 symmetry (**1**, **2**) and one, at lower energy.[2] has full tetrahedral T_d symmetry (**3**). There are experimental[2] and theoretical[2,3] indications that the tetrahedral isomer should behave as a tetravalent 'superatom'. Experiments on laser co-vaporisation of uranium oxide and graphite are interpreted as indicating a trapping by the cage of one atom of uranium. leading to stabilisation of the T_d carbon framework. Attachment of four hydrogen atoms to the exterior of the cage is predicted to give a stable, closed-shell hydride $C_{28}H_4$ with retention of tetrahedral symmetry.[2] Various hypervalent molecules have been proposed in which the cage encloses a transition-metal atom, with or without external hydrogenation.[3] Kroto and Walton[4] suggest that all fullerenes C_n will have characteristic valencies and that it should be possible to build up a generalised periodic table of fullerene superatom chemistry on this basis.



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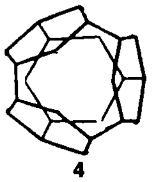

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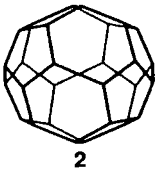

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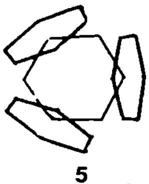

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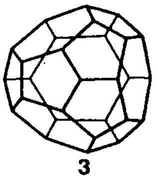

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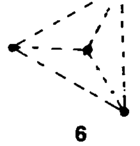

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Qualitative rationalisation of these results follows from simple Hückel theory. In the simplest version of the model all atoms (bonds) are assigned equal α (β) parameters. The π energy levels of the cage **3** are shown at the right side of Fig. 1; 16 of them are bonding and 12 are antibonding. The HOMO is a set of four degenerate bonding orbitals with symmetries a_1 and t_2 in T_d, and therefore the Hückel ground state of C_{28} is the high-spin $^5A_2$ term of the open-shell $a_1^1t_2^3$ configuration. Addition of four electrons, either from an encapsulated atom or from substituents at the corners of the master tetrahedron, or removal of four electrons from the π system by formation of σ bonds. allows completion of a closed-shell electronic configuration, hence the expected stability[2] of U@C_{28} and $C_{28}H_4$.

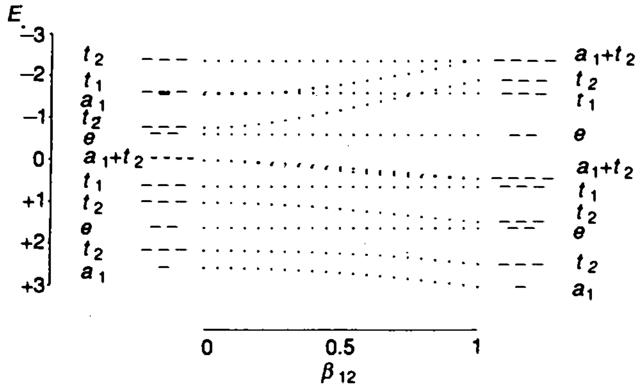

Fig. 1 Energy levels of the π system of C_{28}. E is the energy measured in units of β from the origin α (non-interacting atoms), and β_{12} is a reaction coordinate for the formation of C_{28} (**3**) by simultaneous capping of all four open faces of C_{24} (**4**). The right-hand set of energy levels $E = \alpha - x\beta$ corresponds to C_{28} with all α and β parameters equal. and the characteristic equations for each symmetry are: $(x + 3)(x^2 - 2x - 1) = 0$ (a_1): $(x^2 - x - 1) = 0$ (e): $(x^2 + x - 1) = 0$ (t_1): $(x^2 - 2x - 1)(x^3 + 2x^2 - 4x - 7) = 0$ (t_2). so that the energies in ascending order are $(E - \alpha)/\beta = 3$ (a_1), 2.4728 (t_2). 1.6180 (e). 1.4626 (t_2). 0.6180 (t_1). 0.4142 ($a_1 + t_2$) (the HOMO). −0.6180 (e). −1.6180 (t_1), −1.9354 (t_2). −2.4142 ($a_1 + t_2$). The left-hand stack of levels refers to the opposite limit where the four capping atoms have $x = 0$ and the 24 cage atoms give orbital energies $E = \alpha - x\beta$ obeying: $(x^2 + x - 4) = 0$ (a_1): $(x + 1)(x^3 - x^2 - 5x + 4) = 0$ (t_2). and with explicit energies $(E - \alpha)/\beta =$ 2.5616 (a_1). 2.1643 (t_2). 1.6180 (e). 1 (t_2). 0.6180 (t_1), −0.6180 (e). −0.7729 (t_2). −1.5616 (a_1), −1.6180 (t_1). −2.3914 (t_2). At any value of β_{12}, e and t_1 levels are of constant energy and obey the C_{28} characteristic equations. At intermediate values the HOMO is split, with a_1 lying above t_2. Although the highest antibonding energy appears constant on this scale, it varies slightly with β_{12}.

The attachment of hydrogens in T_d $C_{28}H_4$ is at the four points where three pentagons meet[2] and form pyramidal sites suitable for sp^3-hybridised C–H carbon atoms. This steric factor presumably reinforces the electronic stabilisation arising from shell closure. A related prediction is that occupation of the same sites by nitrogen atoms would also lead to a local minimum on the potential surface for $C_{24}N_4$, giving a molecule with four *exo* lone pairs that is isoelectronic with C_{28}^{4-}.

Semi-empirical calculations on $C_{24}N_4$ using three methods (AM1, PM3 and MNDO) yield the optimised structure shown in Fig. 2. The maximal T_d symmetry is maintained and all three Hamiltonians yield essentially the same geometry which is in agreement with simple ideas about the electronic structure. The four hexagonal faces are fully benzenoid in character (planar regular hexagons, with internal angles 120 ± 0.7° and bond lengths ~ 1.42 Å) though this is not forced by the tetrahedral symmetry. The four carbon atoms of each pentagon are also coplanar, with a length of ~ 1.50 Å for the hexagon–hexagon edge, typical of a single bond. The four nitrogen atoms are raised out of the pentagonal plane at CN distances ~ 1.49 Å, with a pyramidal angle of ~ 102° which is smaller than in typical

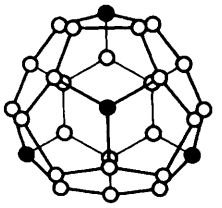

Fig. 2 Optimised structures of $C_{24}N_4$. The filled circles represent N atoms and the two sets of 12 equivalent carbon atoms are denoted by empty circles. Five geometric parameters are needed to specify this structure in general, but this is reduced to three by the fact that the hexagons are predicted to be planar and regular within the precision of the optimisation. The three remaining independent bond lengths are CN [1.50 Å (AM1), 1.49 Å (PM3), 1.48 Å (MNDO)], CC linking hexagons [1.51 Å (AM1), 1.49 Å (PM3), 1.49 Å (MNDO)], CC hexagonal edges [1.42 Å (AM1), 1.42 Å (PM3), 1.43 Å (MNDO)]. The distances from the centre of mass to a hexagon centre are 1.93 Å (AM1), 1.92 Å (PM3), 1.93 Å (MNDO), and to a nitrogen atom they are 2.66 Å (AM1), 2.61 Å (PM3), 2.62 Å (MNDO). Pyramidal angles at the nitrogen centres are 101° (AM1), 103° (PM3), 103° (MNDO).

tertiary amines and possibly indicative of some residual steric strain. Diagonalisation of the Hessian matrix at the optimal structure for each method gave a lowest (triply degenerate) vibrational frequency in the range 414 ± 16 cm^{-1} for the normal isotopomer, confirming that this structure is a true minimum for $C_{24}N_4$.

To aid interpretation of the electronic structure of C_{28} and its derivatives, it is instructive to take apart the C_{28} cage in stages. If we remove the four apical atoms, the remaining structure **4** is a tetrahedral array of four hexagons, each linked at 1, 3 and 5 positions to the three others. The 24-atom structure also represents the 24-electron π system left behind when the apical carbons are saturated or replaced by tertiary nitrogens. It has 12 bonding and 12 antibonding orbitals (left side of Fig. 1), the origin of which becomes evident when the deconstruction of the cage is taken a step further. Cutting the hexagon–hexagon links in the π system leaves **5**, a set of four isolated six-membered rings capable of holding six bonding electrons each. These benzenoid rings survive intact in **4**, with a π bond order of 0.623 along each interior edge and only 0.366 along the external links. The total π energy of $24\alpha + 34.2889\beta$ for **4** indicates a stabilisation of 2.2899β over the isolated rings.

With the full 28-atom framework in place, the isoelectronic C_{28}^{4+} system has positive charge on the apical atoms ($\delta+ = 0.388$), but the bulk of the positive charge is on the hexagonal rings ($\delta+ = 0.612$). The π bond order is 0.553 within the hexagons and only 0.272 between them, but the bonds to the apical atoms have bond order 0.416. In the Hückel picture, then, removal/saturation of the apex atoms causes electronic charge to flow into the rings, stabilising the delocalised π system. The calculated SCF bond lengths in $C_{28}H_4$ and C_{28} are consistent with this picture.[2]

These results all follow from the pattern of Hückel energy levels for C_{28}, but a minor puzzle remains. Why is there a four-fold degeneracy of the HOMO level at $\varepsilon = \alpha + (\sqrt{2} - 1)\beta$? Within T_d the maximal degeneracy of an irreducible representation is three and, as we have seen, the HOMO of neutral C_{28} is actually a coincidence of singly and triply degenerate levels. Such 'accidental' degeneracies are common in Hückel eigenvalue spectra, and often represent an additional substitutional symmetry of the framework, without necessarily implying a symmetry group higher than the apparent point group.[5] In the present case, use of a more sophisticated Hamiltonian within the constraints of T_d symmetry lifts the degeneracy. First-order perturbation analysis shows that it is sufficient to allocate different α parameters to the three symmetry-distinct sets of atoms (α_1 to the apices, α_2 to their immediate neighbours, and α_3 to the other 12 atoms in hexagonal faces) or different β parameters to the three symmetry-distinct sets of bonds (β_{12} to the 12 bonds to apices, β_{23} to the 24 hexagon sides, and β_{33} to the 6 hexagon–hexagon links) to separate the a_1 and t_2 orbital energies, so the degeneracy is truly accidental. At the equal-parameter limit for neutral C_{28} the HOMO energies vary in first-order with changes in the Hückel parameters as

$$\Delta E^{(1)}(\alpha_1) = \frac{12 + 3\sqrt{2}}{28}\Delta\alpha_1 + \frac{8 - 5\sqrt{2}}{28}\Delta\alpha_2 + \frac{4 + \sqrt{2}}{14}\Delta\alpha_3 + \frac{-6 + 9\sqrt{2}}{14}\Delta\beta_{12} + \frac{-6 + 2\sqrt{2}}{7}\Delta\beta_{23} + \frac{4 + \sqrt{2}}{14}\Delta\beta_{33}$$

$$\Delta E^{(1)}(t_2) = \frac{12 + 7\sqrt{2}}{92}\Delta\alpha_1 + \frac{24 - 9\sqrt{2}}{92}\Delta\alpha_2 + \frac{28 + \sqrt{2}}{46}\Delta\alpha_3 + \frac{2 + 5\sqrt{2}}{46}\Delta\beta_{12} + \frac{-22 + 14\sqrt{2}}{23}\Delta\beta_{23} + \frac{-4 + 13\sqrt{2}}{46}\Delta\beta_{33}$$

so that the splitting is

$$\Delta E^{(1)}(a_1 - t_2) = 0.3421\Delta\alpha_1 - 0.0893\Delta\alpha_2 - 0.2527\Delta\alpha_3 + 0.2834\Delta\beta_{12} - 0.3574\Delta\beta_{23} + 0.0740\Delta\beta_{33}$$

predicting, for example, that the a_1 level will lie above t_2 for weak β_{12} links and above it when electronegative atoms are substituted at the apices. A splitting can also be induced by replacing the Hückel Hamiltonian with a more realistic semi-empirical Hamiltonian that takes nearest-neighbour interactions into account. If the splitting were to become large enough to overcome the pairing energy, then a ground state of lower multiplicity (and with a Jahn–Teller distorted equilibrium geometry) would be predicted. The ground state remains $^5A_2$ at the spin-restricted SCF level of theory in a double-zeta basis set and with a fixed tetrahedral geometry.[2]

The fact that the HOMO set consists of $(a_1 + t_2)$ orbitals can be rationalised by reversing the deconstruction and imagining C_{28} to form from C_4 and C_{24}. When structure **4** is capped by four atoms approaching along the tetrahedral C_3 axes, the π orbitals of the 24-atom fragment **4** span $2a_1 + 2e + 2t_1 + 4t_2$, and those of the capping atoms **6** span $a_1 + t_2$. The π orbitals of the full C_{28} framework therefore span $3a_1 + 2e + 2t_1 + 5t_2$. All e and t_1 energies are common to **3** and **4** and so are constant along the capping reaction coordinate. Interaction between the orbitals of the capping atoms and equisymmetric orbitals of the C_{24} fragment causes the bonding and antibonding energies to split apart in both a_1 and t_2 manifolds, introducing an extra bonding orbital set in each symmetry. The frontier orbitals of the full cluster have the symmetries of the orbitals of the capping atoms. These MOs span the same symmetry as four non-interacting 'dangling bonds',[2] and the accidental four-fold degeneracy occurs only at the limits of $\beta_{12} = 0$ (no interaction) and $\beta_{12} = 1$ (all bond parameters equal) of the capping reaction coordinate (see Fig. 1). At $\beta_{12} = 1$ the highest antibonding orbital set also has an $a_1 + t_2$ degeneracy, and crossings of $a_1 + t_1$ and $t_1 + t_2$ levels occur at intermediate values of β_{12}.

In the neutral C_{28} cluster with all bond parameters equal, the spin distribution (the charge distribution of the HOMO) is 0.324 electrons on each apex atom, and 0.676 electrons per hexagonal ring, so that the radical is to some extent stabilised by delocalisation of the HOMO and C_{28} can be regarded as a 3D analogue of triphenylmethyl, Gomberg's radical.[6]

The essential features of the electronic structure of C_{28} and its derivatives are thus implicit in the crude but effective Hückel model of qualitative molecular orbital theory.

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