Supplementary Material (ESI) for New Journal of Chemistry


# ELECTRONIC SUPPLEMENTARY INFORMATION

## Structural and conformational study of two solvates of a fulgenic acid derivative

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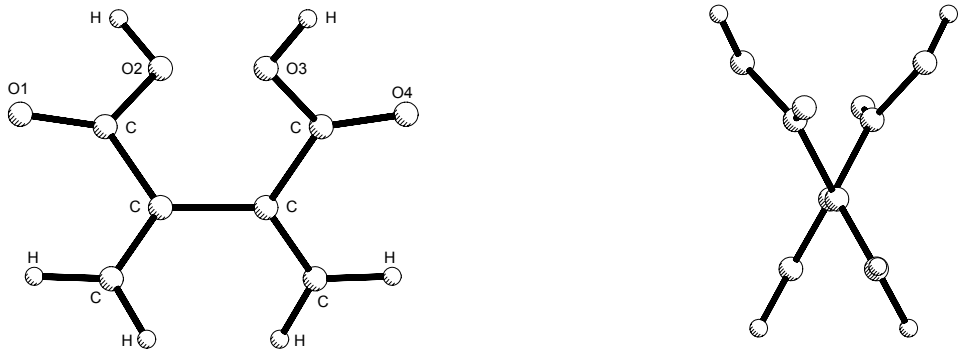
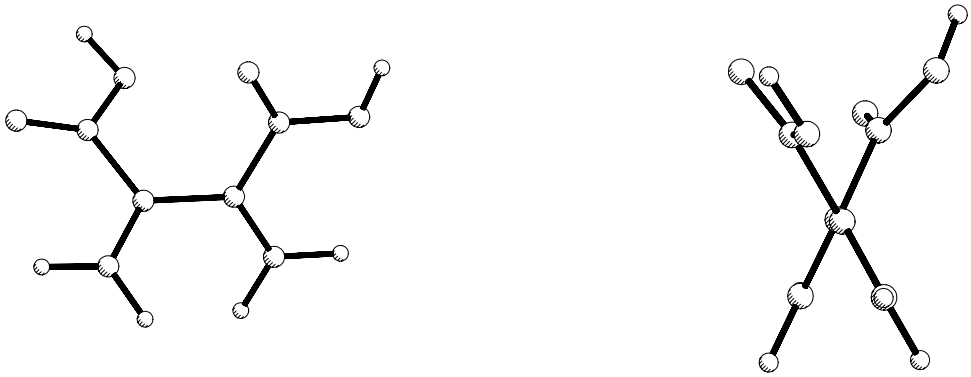
## A1

Two views of the optimised geometry of model A with the arrangement of carboxylic groups yielding lowest energy. Global energy minimum, ZPE-corrected energy value:
E = -533.025785 Hartrees (a.u.).
O2 … O3 distance: 2.994 Å. Value of dihedral angle δ = 55.0° (the δ angle, defined in the text, is formed by atoms of the butadienic chain).




## A2

Optimised geometry of model A, with alternative arrangement of carboxylic groups with respect to that of A1. E = -533.025484 a.u., 0.19 kcal $mol^{-1}$ above A1.
Closest O … O approach: 3.017 Å. δ dihedral angle: 52.2°.



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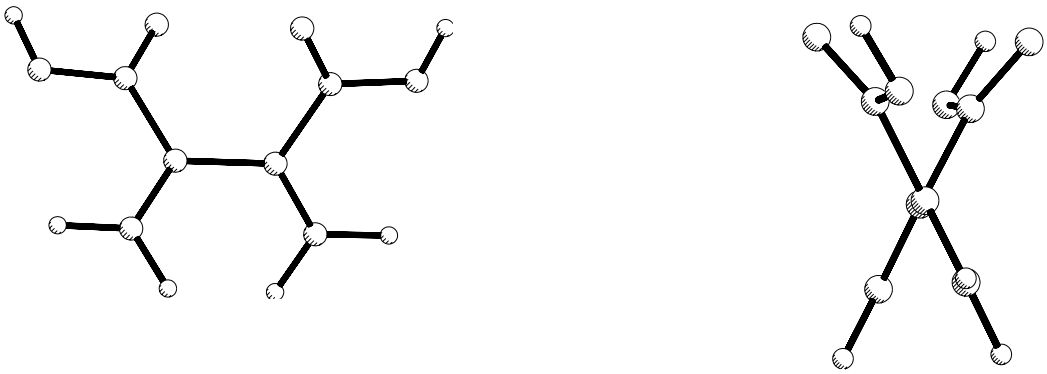
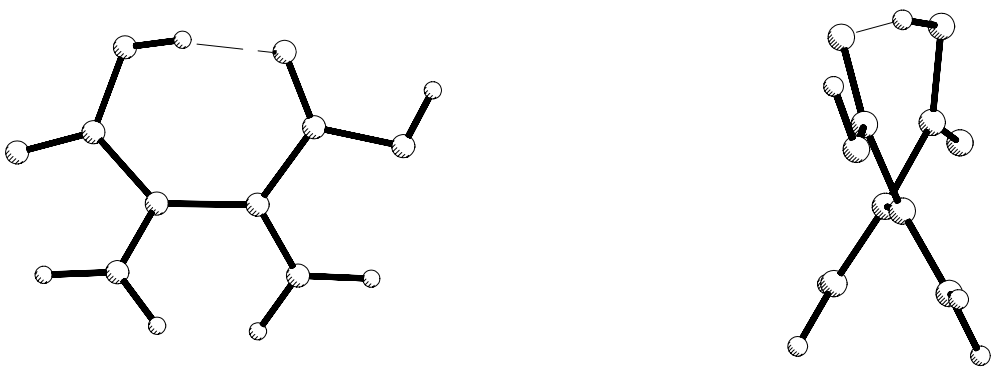
# A3

Optimised model A geometry with the third type of carboxyls arrangement.
E = -533.025107 a.u., 0.43 kcal $mol^{-1}$ above A1.
Closest O … O approach: 3.090 Å. δ dihedral angle: 50.0°.



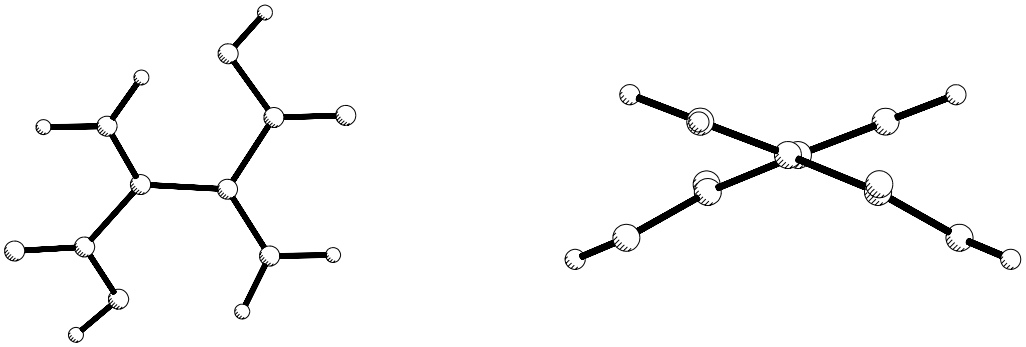
# A4

Model A with intramolecular hydrogen bond. E = -533.022771 a.u., 1.89 kcal $mol^{-1}$ above A1, or 1.70 kcal $mol^{-1}$ above the energy of the more directly related A2 arrangement.
O … O distance 2.671 Å. δ = 55.5°.



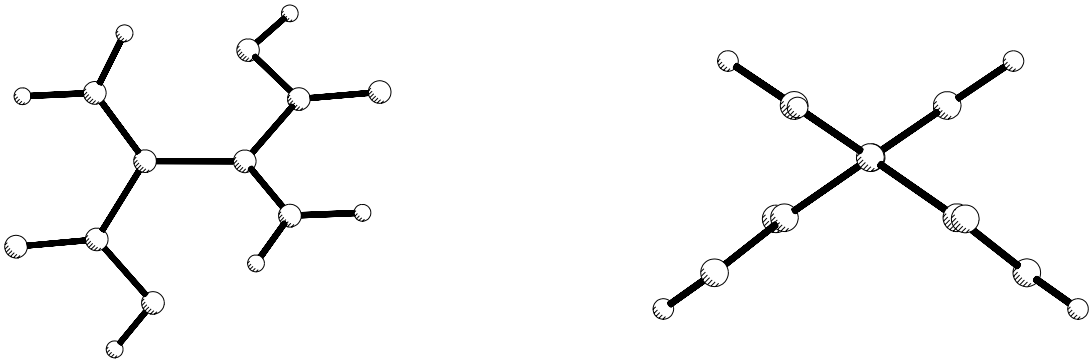
# A5

Relative minimum energy geometry of model A, reached from A1 through rotation around the $C_\alpha$- $C_{\alpha'}$ bond. E = -533.022207 a.u., 2.25 kcal $mol^{-1}$ above A1. $\delta$ = 136.2°.



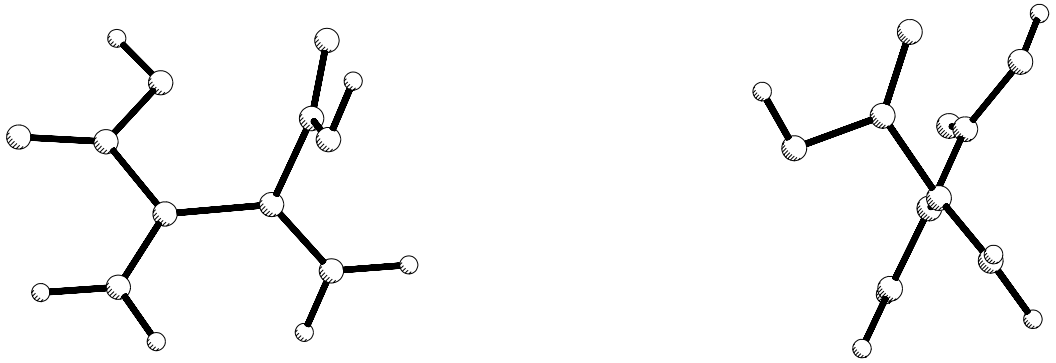
# A6

Geometry at the transition state along the path between minima A1 and A5, connected by rotation around the $C_\alpha$- $C_{\alpha'}$ bond. E = -533.022024 a.u., 2.36 kcal $mol^{-1}$ above A1. $\delta$ = 111.1°.



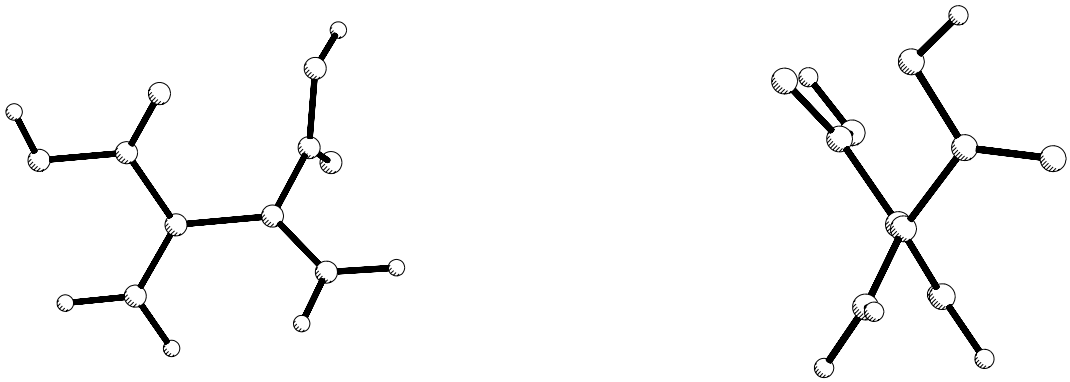
# A7

Geometry at one of the transition states of model A, for rotation of a carboxylic group around its C- $C_\alpha$ bond. E = -533.013906 a.u., 7.45 kcal $mol^{-1}$ above A1. $\delta = 59.9°$.



# A8

Geometry at one of the transition states (alternative path with respect to that of A7) of model A, for rotation of a carboxylic group around its C- $C_\alpha$ bond. E = -533.013034 a.u., 8.00 kcal $mol^{-1}$ above A1. $\delta = 59.8°$.



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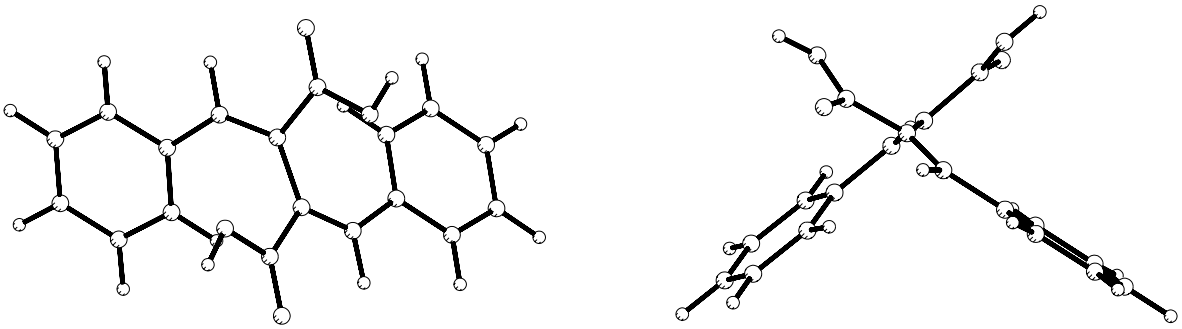
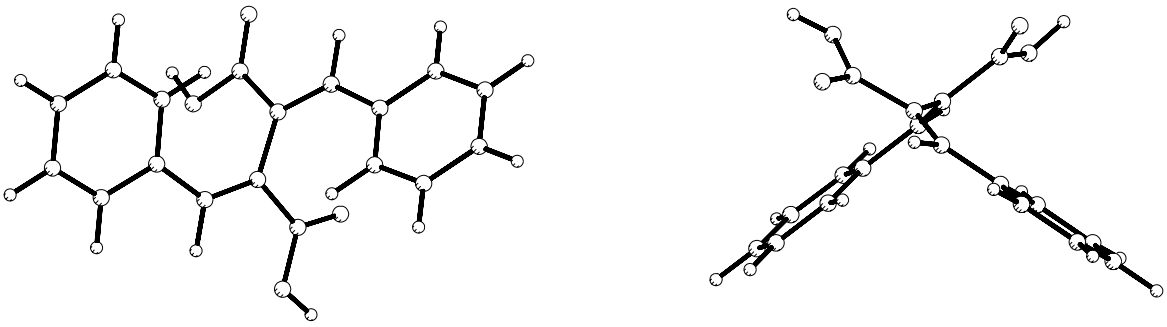
# B1

Geometry at the global energy minimum of model B: should be compared with those in Figures 1 and 3 of the text. E = -994.993914 a.u. (non ZPE-corrected value -995.273239 a.u., for further reference). Closest O … O approach: 3.732 Å. δ = 109.8°.



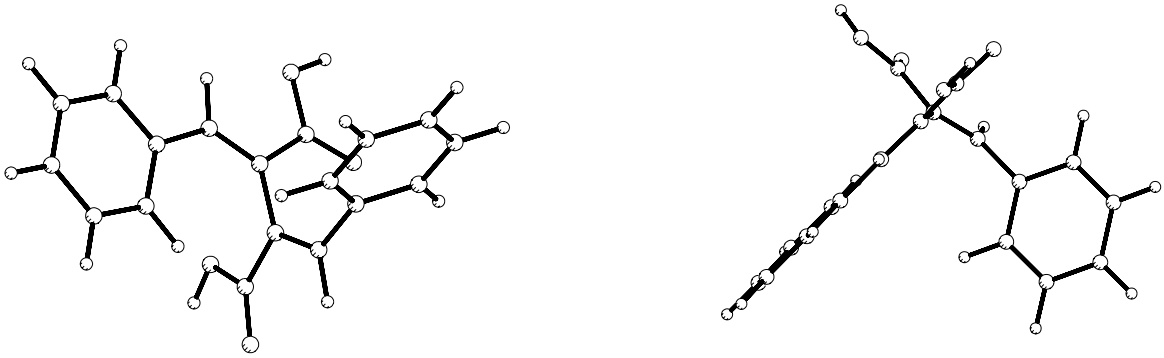
# B2

Relative minimum energy geometry of model B, differing from that of B1 in the arrangement of the carboxylic hydrogens. E = -994.992196 a.u., 1.08 kcal $mol^{-1}$ above the energy of B1. Closest O … O approach: 3.851 Å δ = 113.3°.



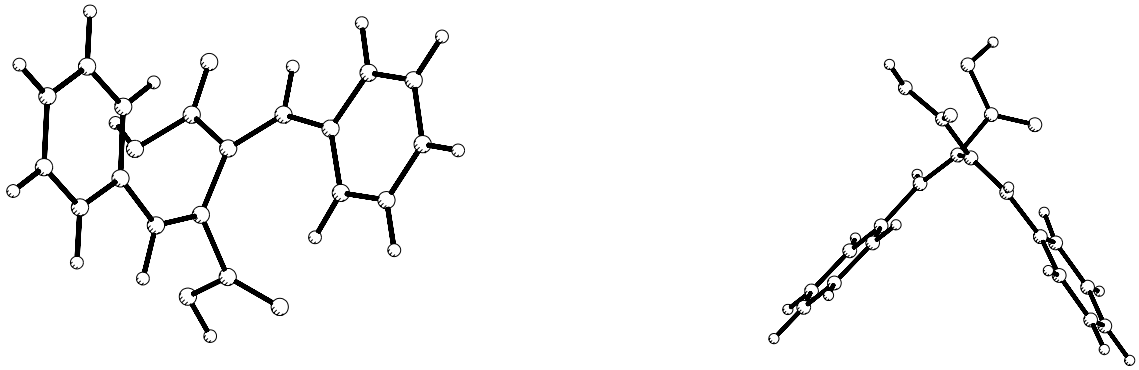
# B3

Transition state geometry for the process of rotation of a phenyl group around the $C_\beta$-$C_\gamma$ bond in model B (labels of carbon atoms are given in the Scheme in the text). E = -994.987204 a.u., 4.21 kcal mol$^{-1}$ above the energy of B1, and 3.31 kcal mol$^{-1}$ above that of B2, to which the geometry of the TS B3 is more closely related. $|\delta|$ = 96.3°.



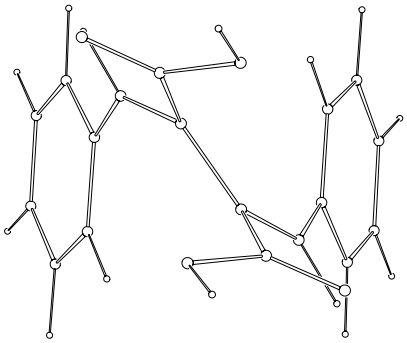
# B4

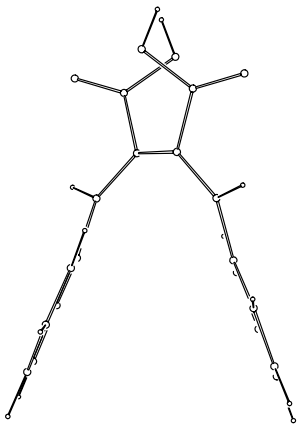
Transition state geometry for the process of rotation of a carboxylic group around its C-$C_\alpha$ bond in model B. E = -994.982042 a.u., 7.45 kcal mol$^{-1}$ above the energy of B1. $\delta$ = 87.9°.



# B5

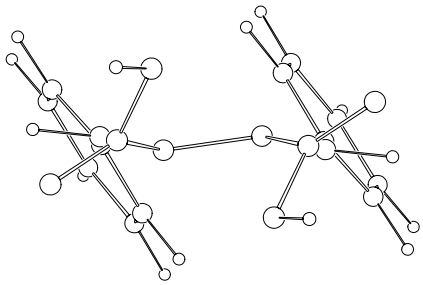
Conformation attained at $\delta = 50.0°$ by the model molecule B, along a path of restrained geometry optimisations at fixed values of the dihedral angle $\delta$, corresponding to rotation around the $C_\alpha$-$C_{\alpha'}$ bond. The appreciable departure from planarity of each half part of the molecule may be noticed. E = -995.26976 a.u., 2.2 kcal $mol^{-1}$ above the non ZPE-corrected energy of B1. This and following energy values for B are not corrected for ZPE, whose value is not available for restrained optimisations.

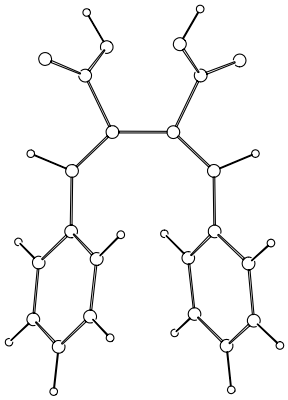




# B6

Two views of the geometry of model B in proximity of the saddle point along the -$\delta$ path of restrained geometry optimisations, performed by rotation about the $C_\alpha$-$C_{\alpha'}$ bond for decreasing values of the $\delta$ hinge angle. E = -995.22401 a.u., 30.9 kcal $mol^{-1}$ above the ZPE-uncorrected energy of B1. $\delta = -40°$.





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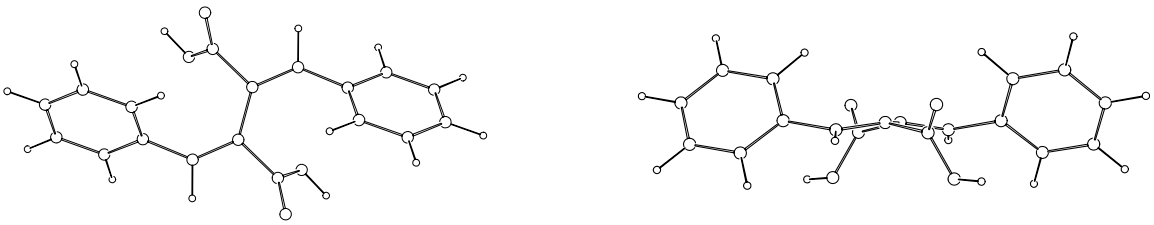
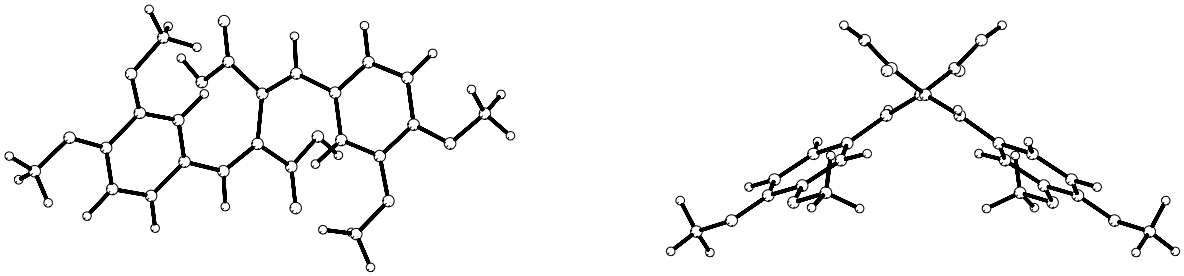
# B7

Two views of the geometry of model B in proximity of the saddle point along the +δ path of restrained geometry optimisations, performed applying rotations about the $C_\alpha$-$C_{\alpha'}$ bond for increasing values of the δ hinge angle. E = -995.24155 a.u., 19.9 kcal mol$^{-1}$ above the ZPE-uncorrected energy of B1. δ = 200° (or -160°).



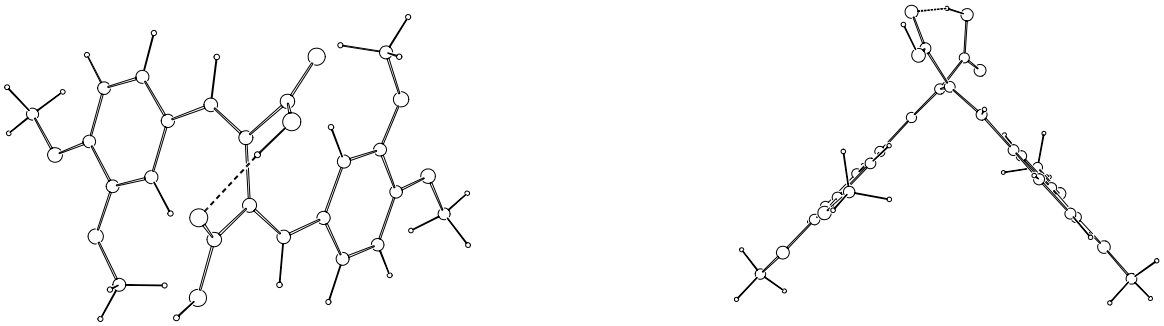
# C1

Geometry at the global energy minimum of model C, to be compared with the geometry of B1 and those in Figures 1 and 3 of the text. E = -1452.959434 a.u. (non ZPE-corrected value for later reference: -1453.369691 a.u.). Closest O … O approach: 3.748 Å. δ = 113.6°.



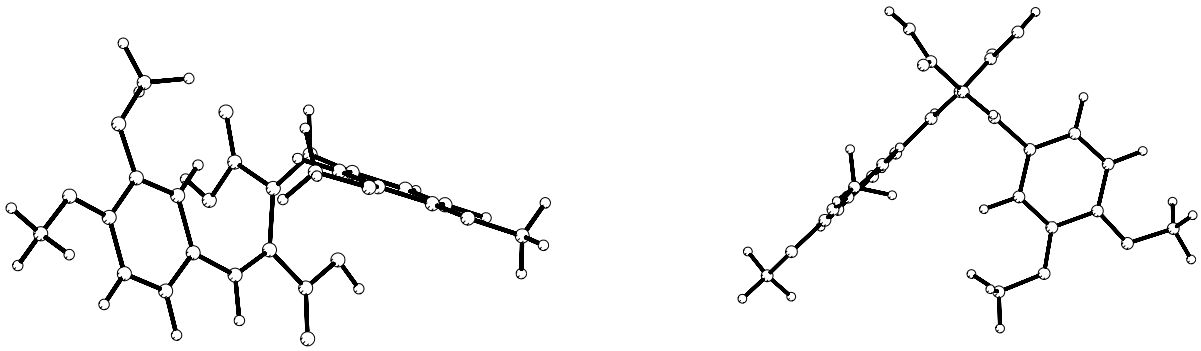
# C2

Model C with intramolecular hydrogen bond. E = -1452.956933 a.u., 1.57 kcal $mol^{-1}$ above the energy of C1. O … O distance 2.746 Å. $\delta = 84.1°$.



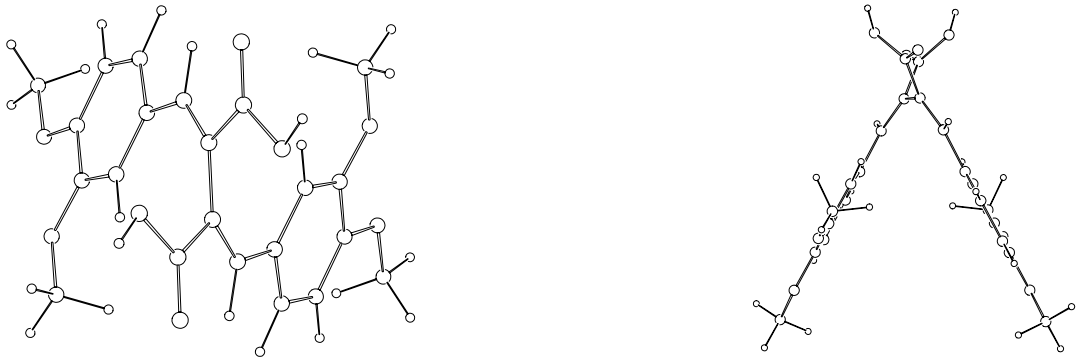
# C3

Transition state geometry for the process of rotation of a phenyl group around the $C_\beta$-$C_\gamma$ bond in model C (labels of carbon atoms as in the Scheme in the text). E = -1452.949913 a.u., 5.97 kcal $mol^{-1}$ above the energy of C1. $\delta = 94.0°$.



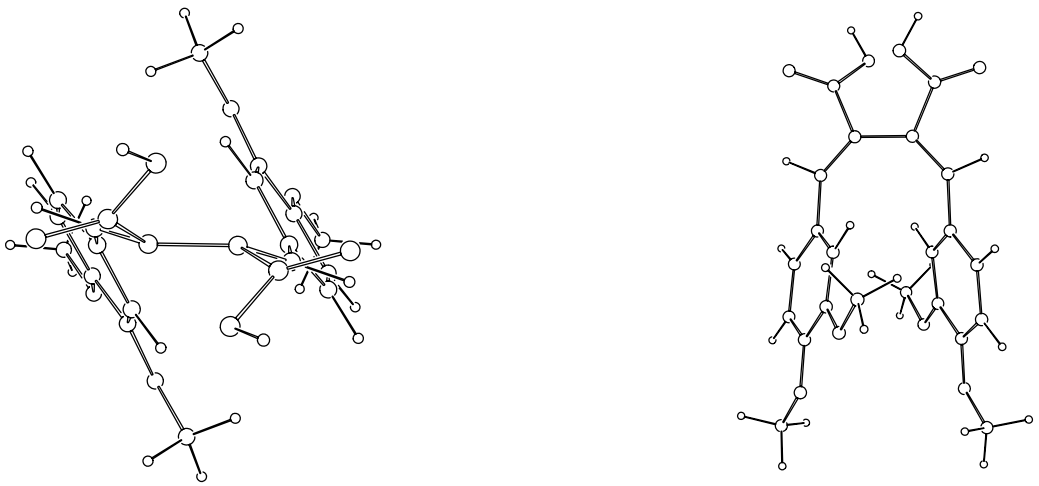
# C4

Conformation attained at $\delta = 50.0°$ by model C, along a path of restrained geometry optimisations at fixed values of the dihedral angle δ, corresponding to rotation around the $C_\alpha$-$C_{\alpha'}$ bond. As for B (B5), partial loss of planarity in the two parts of the molecule (cinnamic backbones) is evident. E = -1453.364254 a.u., 3.4 kcal $mol^{-1}$ above the ZPE-uncorrected energy of C1.



# C5

Two views of the geometry of model C in proximity of the saddle point along the -δ path of restrained geometry optimisations, performed by rotation about the $C_\alpha$-$C_{\alpha'}$ bond for decreasing values of the δ hinge angle. E = -1453.315554 a.u., 34.0 kcal $mol^{-1}$ above the ZPE-uncorrected energy of C1. $\delta = -40°$.



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# C6

Two views of the geometry of model C in proximity of the saddle point along the +δ path of constrained geometry optimisations, performed applying rotations about the $C_\alpha$-$C_{\alpha'}$ bond for increasing values of the δ hinge angle. E = -1453.330813 a.u., 24.3 kcal $mol^{-1}$ above the ZPE-uncorrected energy of C1. δ = 210° (or -150°).