

Molecular structure and reactions of 1,1'-bi(acenaphthen-1-ylidene)-2,2'-dione

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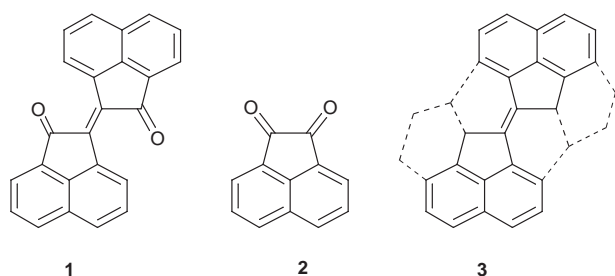
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The molecular structure of 1,1'-bi(acenaphthen-1-ylidene)-2,2'-dione **1**, a potential building-block for the synthesis of fullerene fragments, has been investigated by X-ray crystallography and semi-empirical (AM1 and PM3) calculations. There is a good agreement between the calculated and crystal structure which is essentially planar and has *E*-configuration. In the solid state, molecules of **1** pack in an interesting manner as corrugated sheets sustained by a network of C–H···O hydrogen bonds and resulting in the formation of tetrameric loops. While steric factors limit the reactivity of the carbonyl groups in **1**, the ene double bond of the ene-dione moiety present in it exhibits propensity toward [4 + 2]-cycloadditions to furnish novel and highly compressed polycycles **8–10**.

As a part of an ongoing programme¹ directed towards the synthesis of C₆₀ and its fragments through classical synthetic approaches, we became interested in identifying suitable building blocks that were rich in carbon content, had a generous complement of 5- and 6-membered rings that mapped directly onto the fullerene surface and bore sufficient functionalization for further elaboration to bucky-bowls. In this context, our attention was drawn to 1,1'-bi(acenaphthen-1-ylidene)-2,2'-dione **1**, a bright orange compound known for over fifty years



and readily available from acenaphthenequinone **2**.² The C₂₄H₁₂O₂ compound **1**, with six rings, is particularly well suited for evolution to many fullerene fragments, like C_{2v} symmetry C₃₀-semifullerene (see **3**),³ through the appropriate homologation of the carbonyl functionalities. Despite the ready availability of **1**, its chemistry has not received any attention and even its *anti*- or (*E*)-configuration has been presumed on the basis of steric considerations.² Thus, prior to the utilization of **1** in our projected synthesis, it was necessary to elucidate its molecular structure and probe its reactivity. Of particular concern was the steric environment in the vicinity of the carbonyl groups and the extent of the twisting and/or pyramidalization present on the central double bond of the ene-dione moiety. It is to be noted that several systems related to **1** like the overcrowded bistricyclic enes^{4a} bifluorenylidenes,^{4b} dioxantheny-

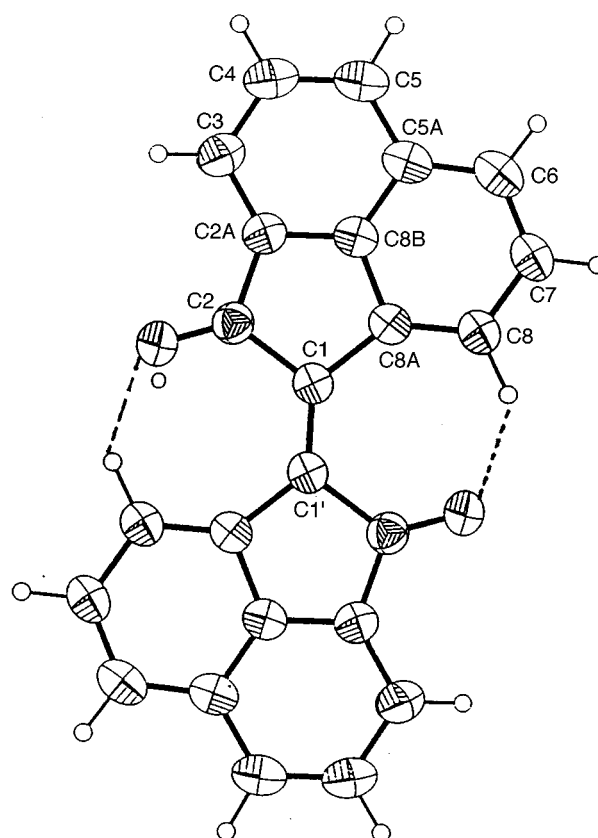


Fig. 1 ORTEP diagram of **1**.

idene^{4c} and 2-(xanthen-9-ylidene)indane-1,3-dione,^{4d} having an overcrowded tetrasubstituted ene moiety exhibit geometrical distortions. Herein, we describe the X-ray and calculated molecular structure of **1** as well as some selected reactions of this interesting ring system.

Crystal and molecular structure of **1**

The molecular structure of **1** is shown in Fig. 1, which indicates

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that it crystallizes as the (*E*)-isomer and has a centre of symmetry. There are two molecules in the unit cell. Furthermore, each acenaphthenylidene moiety in **1** is essentially planar. The angles between the planes of the five-membered ring and the six-membered rings are 1.3° and 1.5° and the angle between the planes of the two six-membered rings is 0.4°. The carbon atoms of the central ene bond are not pyramidalized. The C1–C1' bond length is 1.368(3) Å and the pure twist around C1=C1' is 0.1°. The only significant deviation from planarity appears in the slight tilting of the oxygen atoms from the plane of the carbocyclic moiety: the torsional angles O–C2–C1–C1' and O–C2–C1–C8a are 5.6° and –174.4°, respectively; the torsional angles O–C2–C2a–C3 and O–C2–C2a–C8b are –3.9° and 174.4°, respectively. The above tilting of the oxygen atoms could be attributed to the relatively strong intramolecular C–H···O hydrogen bonding involving the two oxygen atoms and the H8 protons (H···O distance 1.95 Å, C···O distance 2.79 Å and C–H···O angle 134.9°), see Fig. 1.⁵

A look at the packing pattern reveals that **1** has a layered structure⁵ and the interplanar separation is 3.83 Å along the *a* axis (Fig. 2). The packing motif in each of these layers consists of interpenetrating molecules, as shown in Fig. 3, resulting in infinite corrugated sheets. Further, the individual sheets of molecules are held together by an extensive network of inter-

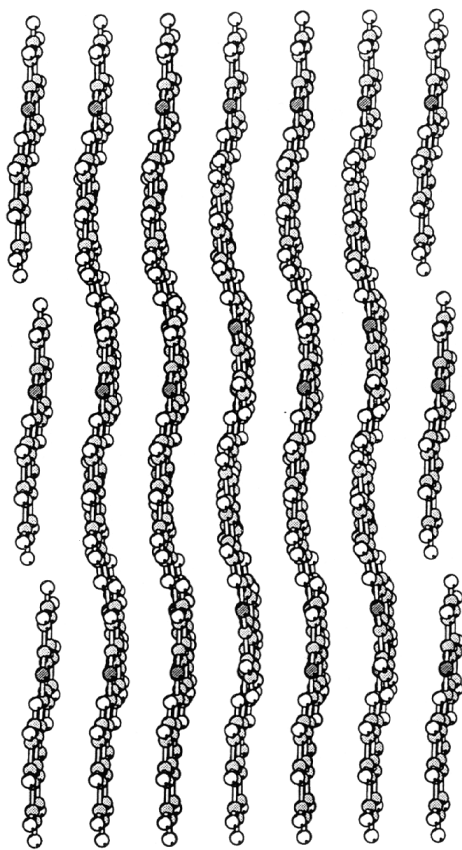


Fig. 2 Packing diagram showing layered structure and corrugated sheets with an interplanar separation of 3.83 Å along the *a* axis.

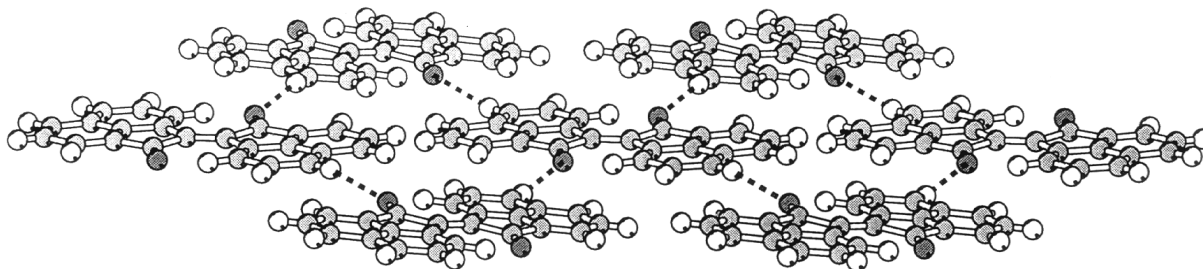
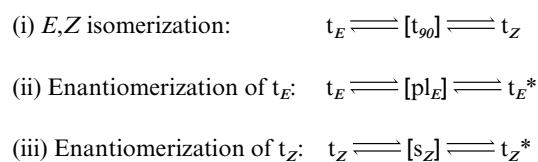


Fig. 3 Packing diagram showing interpenetrating molecules and C–H···O hydrogen bonding within a corrugated sheet.

molecular C–H···O contacts. Each molecule is C–H···O hydrogen bonded through the oxygen atoms and the H6 protons (H···O distance 2.42 Å, C–O 3.35 Å and C–H···O angle of 157.9°) to all four nearest neighbours as depicted in Fig. 4, to define a tetrameric loop. Thus, the oxygen atoms are involved in bifurcated C–H···O hydrogen bonding as they participate both in inter- as well as intra-molecular manner (Fig. 4). In a sense, **1** in the solid state is self-complementary as it possesses both donating sites (through the two H6 protons) and accepting sites (through the two oxygen atoms), enabling it to be involved in quadruple intermolecular hydrogen bonding to define an infinite network with each molecule as a node of a tetrameric loop (Fig. 4).⁵

To complement the X-ray crystal structure determination, calculations were carried out on **1** using the semi-empirical methods PM3 and AM1, as implemented in the MOPAC6 program.⁶ The following conformations of **1** were successfully optimized: *E*-planar (*pl_E*), *Z*-planar (*pl_Z*), *E*-twisted (*t_E*), *Z*-twisted (*t_Z*), *Z*-*syn*-folded (*s_Z*) and orthogonally twisted (*t₉₀*). The *E*- and *Z*-*anti*-folded conformations *a_E* and *a_Z* and *E*-*syn*-folded conformations *s_E* were not found in the conformational space of **1**. The ground states, transition states and local minima were verified by calculations of the frequencies of the various optimized conformations. Table 1 gives the PM3 and AM1 heats of formation, relative heats of formation and selected geometrical parameters of the optimized geometries of **1**. A comparison of the bond lengths, bond angles and dihedral angles of the crystal and the PM3 and AM1 structures of **1** shows that the crystal structure generally resembles the PM3 derived structure more than the AM1 structure. This is especially evident in the torsional angles around C1=C1'.

The calculated minimum of **1** is the *E*-twisted conformation *t_E*. The pure twist (around C1=C1') is only 3.2° (*cf.* 0.1° from the crystal structure data). The *Z*-twisted conformation *t_Z* was found to be a local minimum, 4.2 (PM3) and 3.6 (AM1) kcal mol⁻¹ above *t_E*. It has a substantial pure twist (around C1=C1') of 24.8°. In addition, the following three dynamic processes for **1** were envisioned:



The conformations between the square brackets are the corresponding transition states. The transition state [*t₉₀*] for *E* ⇌ *Z* isomerization is 34.6 kcal mol⁻¹ above *t_E* (PM3). It is close to the orthogonally twisted ene: its pure twist around C1=C1' is almost 89.7°. The transition state for the enantiomerization of *t_E* is the *E*-planar conformation [*pl_E*]. It is only 0.013 kcal mol⁻¹ higher in energy than *t_E* (PM3), suggesting that the deviation from planarity may be an artefact. In AM1, *pl_E* is a third order saddle point 2.3 kcal mol⁻¹ above *t_E*. The transition state for the enantiomerization of *t_Z* is the *Z*-*syn*-folded conformation [*s_Z*]. It is 3.2 and 7.5 (PM3) kcal mol⁻¹ higher in energy than *t_Z* and *t_E*, respectively.

Table 1 Semiempirical PM3 and AM1 heats of formation and selected geometric parameters of optimized conformations of 1,1'-bi(acenaphthen-1-ylidene)-2,2'-dione **1**

Conformation ^a	Symmetry	ΔH_f° kcal mol ⁻¹	$\Delta\Delta H_f^\circ$ kcal mol ⁻¹	Pure twist ^b (°)	χ^c (C1) (°)	Distance/Å						
						H8-H8'	C8-C8'	O-O'	H8-O'	C1-C1'		
<i>PM3 optimization</i>												
t _E	GM	C ₂	60.010	0.0	3.2 ^d	2.0	6.001	5.796	5.440	1.806	1.351	
t _Z	LM	C ₂	64.255	4.245	24.7	0.2	1.728	3.207	2.722	5.474	1.349	
pl _E	TS	C _{2h}	60.023	0.013	0.0	0.0	6.008	5.801	5.451	1.802	1.351	
pl _Z	SP3	C _{2v}	67.882	7.872	0.0	0.0	1.556	3.378	2.088	5.778	1.352	
s _Z	TS	C _s	67.468	7.458	0.0	7.6	1.597	3.365	2.125	5.740	1.348	
t ₉₀	TS	C ₂	94.643	34.633	89.7	0.0	4.182	4.442	4.143	4.085	1.428	
<i>AM1 optimization</i>												
t _E	GM	C ₂	83.443	0.0	18.1	4.0	5.957	5.747	5.322	2.093	1.348	
t _Z	LM	C ₂	87.012	3.569	20.4	2.6	2.018	3.185	2.434	5.513	1.354	
pl _E	SP3	C _{2h}	85.766	2.323	0.0	0.0	6.307	5.920	5.430	1.948	1.354	
pl _Z	SP3	C _{2v}	93.288	9.845	0.0	0.0	1.543	3.351	2.210	5.844	1.353	
s _Z	SP2	C _s	91.590	8.147	0.0	10.8	1.682	3.353	2.294	5.780	1.347	
t ₉₀	TS	C ₂	118.361	34.918	90.0	0.0	4.236	4.491	4.108	4.119	1.418	

^a pl = planar; t = twisted; s = *syn*-folded; t₉₀ = 90° twisted; GM = global minimum; LM = local minimum; TS = transition state; SP_n = saddle point of *n*-th order. ^b The mean of C8A-C1-C1'-C8A' and C2-C1-C1'-C2' dihedral angles. ^c χ (C1), pyramidalization at C1 is the difference between the dihedral angles C2-C1-C1'-C2' and C2-C1-C1'-C8A' ($\pm 180^\circ$). ^d The value obtained from the crystal structure data is 0.1°.

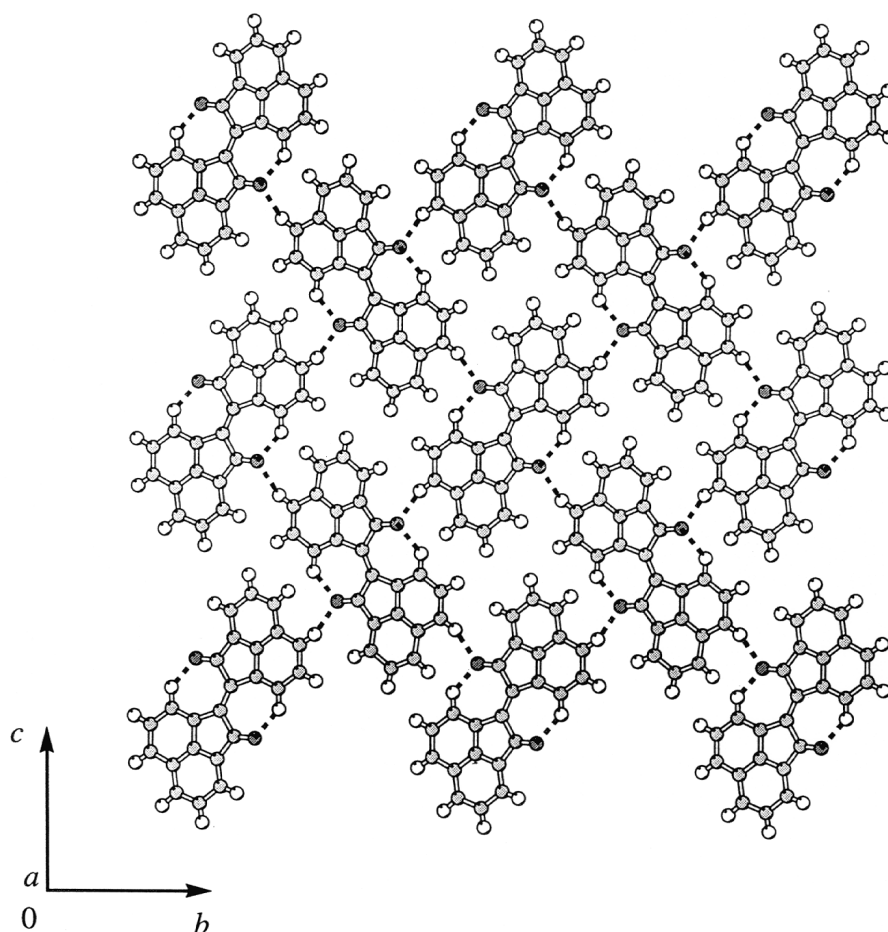
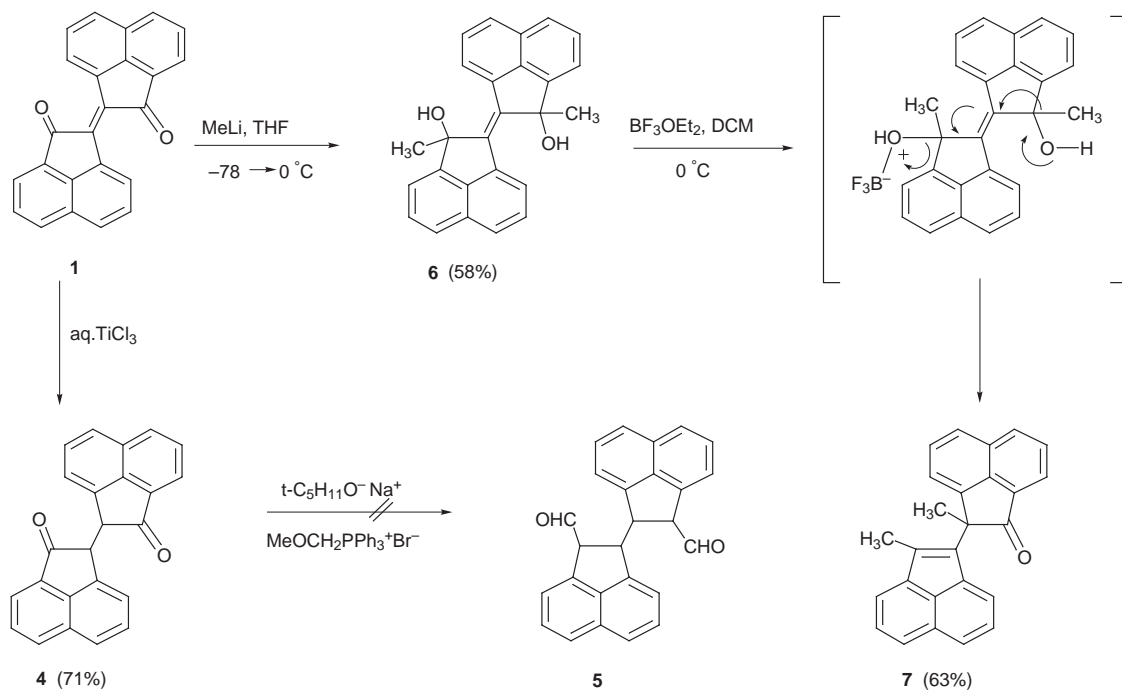


Fig. 4 Crystal packing in **1**, view down *a* axis. Dotted lines represent both inter- and intra-molecular hydrogen bonding and the tetrameric loops are also evident.

Homologation and cycloaddition reactions on **1**

The elucidation of the detailed molecular structure of **1** clearly indicated the sterically encumbered disposition of the carbonyl groups and therefore difficulties in its reactions were anticipated. Nonetheless, we did attempt several Wittig and Wittig-Horner reactions on **1** but without success. However, it was possible to reduce the ene double bond in **1** with aq. Ti^{III} to furnish the dihydro product **4**. However, this compound also

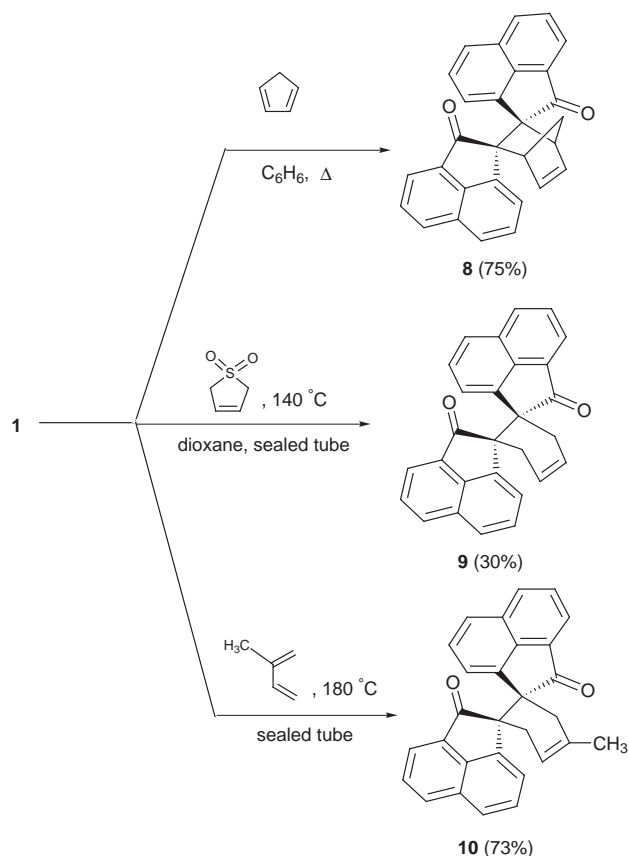
proved to be unreactive towards homologation through Wittig and related reactions and did not furnish the required product **5**. The only reaction that we could effect on the carbonyl groups of **1** was the addition of methyl lithium to furnish the diol **6**. Attempts to dehydrate **6** to the diolefin did not succeed and when Lewis acids like BF₃·OEt₂ were deployed for the purpose, facile cationic rearrangement to the methyl migration product **7** was observed (Scheme 1). Recognising that the carbonyl groups in **1** were not amenable to the projected homologation, we



Scheme 1

decided to probe the dienophilic reactivity of the double bond of the ene-dione moiety. This proved to be more rewarding. Indeed, **1** readily entered into [4 + 2]-cycloaddition with cyclopenta-1,3-diene, buta-1,3-diene and isoprene to furnish Diels–Alder adducts **8–10**, respectively (Scheme 2). Structure of **8–10** were deduced on the basis of their complementary ^1H and ^{13}C NMR data (see Experimental). The adducts **8–10** have two adjacent quaternary carbon centres generated during the Diels–Alder cycloaddition. An indication of the prevailing steric congestion in these adducts is the pronounced deshielding of the olefinic protons in the ^1H NMR spectra. For example, the two norbornene olefinic protons in **8** resonate at δ 6.83 and 7.15 and the cyclohexene protons in **9** are at δ 6.19, approximately 1 ppm downfield from their normal values. The vinylic methyl resonance in **10** is deshielded to δ 1.96 and the two bridge protons of the norbornene moiety in **8** are separated by nearly 2 ppm. Our original intent, somewhat instinctive in retrospect, in preparing the Diels–Alder adducts was to protect the ene moiety in **1**, to enable reactions on the more electrophilic saturated carbonyl groups in adducts **8–10** and then release the products through the retro-Diels–Alder reaction. As it turned out, the highly overcrowded compounds **8–10** were totally refractory towards any chemical reaction.

In summary, we have elucidated the molecular structure of a readily available and seemingly promising compound **1** through X-ray crystallography and semi-empirical calculations. While the carbonyl groups in **1** do not exhibit the expected reactivity towards homologation with Wittig reagents, the tetrasubstituted ene double bond in it displays unexpected propensity towards [4 + 2]-cycloaddition with simple 1,3-dienes to furnish a range of novel, highly compressed polycyclic adducts.



Scheme 2

Experimental

1,1'-Bi(acenaphthen-1-ylidene)-2,2'-dione **1**

This was prepared following the literature procedures described by Rule *et al.*^{2a} and De Jongh *et al.*^{2c} In the former case, acenaphthenequinone **2** was sequentially treated with PCl_5 and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in aq. ethanol. In the later case, the α -diazo ketone derived from **2** via its *p*-tosylhydrazone was thermally decomposed to furnish **1**. Recrystallization of the material obtained in both the cases from nitrobenzene gave red–orange

needles, mp 300 °C; m/z 332 (M^+); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3038, 1699, 1597, 1493, 1001; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 9.48 (2H, d, J 8.8 Hz), 8.18–7.74 (10H, m).

2-(2-Oxo-1,2-dihydroacenaphthyl-1-yl)-1,2-dihydroacenaphthyl-1-one **4**

To the ene-dione **1** (25 mg, 0.076 mmol) in 5 ml of acetone at 0 °C was added 15% aq. TiCl_3 dropwise until a pale purple colour persisted. After stirring at room temperature for 2 h the

reaction mixture was poured into 15 ml of brine solution and extracted with ethyl acetate. The crude material obtained on the removal of the solvent was charged on a silica gel column and elution with 5% ethyl acetate–hexane furnished the reduced product **4** (15 mg, 71%, based on the starting material recovery); mp 256–258 °C; m/z 334 (M^+); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1707, 1599, 819, 775, 644; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 8.14–7.55 (8H, m), 7.12 (2H, t, $J_1 = J_2 = 8 \text{ Hz}$), 6.18 (2H, d, J 8 Hz), 4.85 (2H, s); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 204.3, 142.5, 135.1, 133.8, 131.9, 130.6, 128.1, 128.0, 124.2, 121.7, 120.7, 52.4 (Found: C, 86.15; H, 4.25. $\text{C}_{24}\text{H}_{14}\text{O}_2$ requires C, 86.21; H, 4.22%).

2-(2-Hydroxy-2-methyl-1,2-dihydroacenaphthylen-1-ylidene)-1-methyl-1,2-dihydroacenaphthylen-1-ol **6**

To the ene-dione **1** (180 mg, 0.542 mmol) in dry THF at -78°C , was added MeLi (0.85 ml, 1.41 mmol ml^{-1}) dropwise and the mixture was stirred for 30 min at -78°C . The reaction mixture was stirred for another 2 h at room temperature and then quenched with water and extracted with dichloromethane. The crude reaction product was charged on a silica gel column and elution with 6% ethyl acetate–hexane furnished **6** (98 mg, 58% based on the recovery of starting material); mp 212–213 °C; m/z 364 (M^+); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3518, 3423, 3049, 1365, 1093, 777; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 8.8 (2H, d, J 8 Hz), 7.62–7.39 (10H, m), 2.47 (2H, br s), 1.95 (6H, s); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 148.2, 144.8, 136.1, 135.9, 131.0, 128.5, 127.6, 127.0, 124.9, 124.5, 116.8, 82.2, 25.0 (Found: C, 85.72; H, 5.58. $\text{C}_{26}\text{H}_{20}\text{O}_2$ requires C, 85.68; H, 5.53%).

2-Methyl-2-(2-methylacenaphthylen-1-yl)-1,2-dihydroacenaphthylen-1-one **7**

A catalytic amount of $\text{BF}_3 \cdot \text{OEt}_2$ was added to a cooled (0°C) solution of compound **6** (30 mg, 0.09 mmol) in dichloromethane (5 ml). After 90 min the reaction mixture was quenched with sodium bicarbonate solution and extracted with dichloromethane. The crude product was charged on a silica gel column and elution with 4% ethyl acetate–hexane furnished the rearranged product **7** (18 mg, 63%); mp 116°C ; m/z 346 (M^+); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3749, 1716, 1431, 817, 769; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 8.19 (1H, d, J 8 Hz), 8.09 (1H, d, J 8 Hz), 7.90–7.07 (9H, m), 7.05 (1H, d, J 8 Hz), 2.14 (3H, s); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 207.2, 146.1, 141.6, 140.5, 136.8, 135.7, 132.5, 131.7, 131.0, 129.0, 128.4, 127.9, 127.5, 127.2, 127.1, 125.9, 124.0, 123.7, 122.6, 121.0, 120.7, 56.9, 25.1, 12.3 (Found: C, 90.32; H, 5.24. $\text{C}_{26}\text{H}_{18}\text{O}$ requires C, 90.15; H, 5.23%).

Dispiro[1,2-dihydroacenaphthylene-1,2'-bicyclo[2.2.1]hept-5'-ene-3',1''-(1'',2''-dihydroacenaphthylene)]-2,2''-dione **8**

To a solution of the ene-dione **1** (200 mg, 0.60 mmol) in dry benzene (5 ml) was added an excess of freshly cracked cyclopentadiene and the reaction mixture was refluxed for 10 h. The solvent was removed and the crude product was charged on a silica gel column. Elution with 4% ethyl acetate–hexane furnished the adduct **8** (158 mg, 75% based on the recovery of the starting material); mp $>280^\circ\text{C}$; m/z 333 ($M^+ - 67$); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3063, 2988, 1712, 1263, 1219, 783; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 8.0–7.31 (12H, m), 7.15–7.11 (1H, m), 6.87–6.83 (1H, m), 3.74 (1H, d, J 9 Hz), 3.22 (2H, br s), 1.91 (1H, d, J 9.4 Hz); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 204.1, 203.2, 142.6, 141.5, 141.1, 139.6, 138.9, 136.0, 133.1, 132.8, 131.1, 130.9, 130.0, 129.7, 128.6, 128.3, 127.4, 127.2, 127.1, 125.0, 124.1, 123.8, 120.9, 120.6, 71.7, 69.5, 54.5, 53.8, 47.9 (Found: C, 87.35; H, 4.52. $\text{C}_{29}\text{H}_{18}\text{O}_2$ requires C, 87.41; H, 4.55%).

Dispiro[1,2-dihydroacenaphthylene-1,3'-cyclohexene-4',1''-(1'',2''-dihydroacenaphthylene)]-2,2''-dione **9**

A mixture of ene-dione (29 mg, 0.09 mmol), 3-sulfolene (51 mg, 0.43 mmol) and a pinch of hydroquinone in dioxane (2 ml) was

Table 2 Crystallographic data of 1,1'-bi(acenaphthen-1-ylidene)-2,2'-dione **1**

Molecular formula	$\text{C}_{24}\text{H}_{12}\text{O}_2$
Molecular weight	332.08
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	3.838(1)
$b/\text{\AA}$	13.823(2)
$c/\text{\AA}$	14.166(3)
β ($^\circ$)	93.76(1)
$V/\text{\AA}^3$	749.9(5)
Z	4
ρ (calc.)/ Mg m^{-3}	1.47
μ (Cu-K α)/ m^{-1}	697
No. of unique reflections	1466
No. of reflections with $I \geq 3\sigma(I)$	1194
R	0.043
R_w	0.063

placed in a sealed tube and heated at $130\text{--}140^\circ\text{C}$ for 24 h. The crude reaction mixture was extracted with dichloromethane and after concentration was charged on a silica gel column. Elution with 6% ethyl acetate–hexane furnished the adduct **9** (10 mg, 30%); mp 253°C ; m/z 386 (M^+); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1709, 1494, 1010, 781; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 7.95–7.32 (12H, m), 6.19 (2H, s), 3.06 (2H, d, J 17.4 Hz), 2.68 (2H, d, J 17.4 Hz); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 204.5, 141.4, 141.3, 132.9, 131.5, 130.3, 128.3, 127.8, 125.4, 124.2, 121.5, 121.2, 55.0, 32.6 (Found: C, 87.10; H, 4.65. $\text{C}_{28}\text{H}_{18}\text{O}_2$ requires C, 87.02; H, 4.69%).

1'-Methyldispiro[1,2-dihydroacenaphthylene-1,3'-cyclohexene-4',1''-(1'',2''-dihydroacenaphthylene)]-2,2''-dione **10**

A mixture of the ene-dione (34 mg, 0.1 mmol), isoprene (excess), and a pinch of hydroquinone was heated in a sealed tube at 180°C for 12 h. The crude mixture was extracted with dichloromethane and charged on a silica gel column. Elution with 10% ethyl acetate–hexane furnished the adduct **10** (30 mg, 73%); mp 181°C ; m/z 400 (M^+); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2893, 1709, 1429, 1022, 831, 779; $\delta_{\text{H}}(\text{CDCl}_3; 200 \text{ MHz})$ 7.96–7.27 (12H, m), 5.89–5.88 (1H, m), 2.92–2.66 (4H, m), 1.96 (3H, s); $\delta_{\text{C}}(\text{CDCl}_3; 50 \text{ MHz})$ 204.4, 204.3, 141.5, 141.2, 132.8, 131.5, 130.3, 128.3, 127.7, 124.2, 121.4, 121.2, 119.4, 55.9, 55.1, 37.2, 33.1, 23.5 (Found: C, 87.02; H, 5.05. $\text{C}_{29}\text{H}_{20}\text{O}_2$ requires C, 86.97; H, 5.03%).

X-Ray structure determination of **1**

The X-ray intensity data of **1** were measured on an ENRAF-NONIUS CAD-4 Computer Controlled diffractometer using the θ - 2θ technique to a maximum 2θ of 140° . Cu-K α ($\lambda = 1.54178 \text{ \AA}$) radiation with a graphite crystal monochromator in the incident beam was used. Table 2 gives the crystallographic data of **1** and the ORTEP diagram of the molecular structure is shown in Fig. 1. Lattice parameters were obtained by a least-squares fit of 24 centered reflections in the θ range $27.0\text{--}30.0^\circ$. The intensities of three standard reflections were monitored during data collection, and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The positions of the carbon and oxygen atoms were obtained using the results of the SHELXS-86 direct method analysis.⁷ After several cycles of refinement the positions of the hydrogen atoms were found, and added to the refinement process. The refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$. Further details are provided in the supplementary material. CCDC reference number 207/319. See <http://www.rsc.org/suppdata/p1/1999/1871> for crystallographic files in .cif format.

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