Twisting and planarization in push–pull ethylenes†

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As determined by X-ray crystallography, Meldrum's acid derivatives **8**–**19** feature dihedral angles around the central C=C double bonds between 3 and 83°. Hydrogen bonds between substituents RHN and the carbonyl groups favour near-planarity. Sterically demanding substituents favour large dihedral angles and zwitterionic structures as in formula **20**. AM1 calculations of the structures are in excellent agreement with the experimental X-ray data, provided a dielectric field is incorporated ($\varepsilon = 40$). This can be ascribed to the highly polar (zwitterionic) nature of the molecules. It is further predicted that all these molecules, including those that are stabilised in a planar form by intramolecular hydrogen bonds, undergo rapid rotation about the central C=C bonds at room temperature. DFT calculations incorporating a dielectric field model (PCM) are in excellent agreement with the near-perpendicular arrangement of the alkene moiety in **19**.

Introduction

The rotational barriers around the C=C double bonds in ethylenes substituted with donor and acceptor substituents at the two termini (push–pull ethylenes) are significantly lower than the habitual 65 kcal mol^{-1}.[1] This is usually explained in terms of preferential stabilisation of a zwitterionic (betaine) transition state.[1,2] Furthermore, the molecules may exhibit twisting around the C=C bond in the ground state. Consequently, the ground state itself may possess zwitterionic character. Chart 1 illustrates the twisting angles and C=C bond lengths in a number of such ethylenes **1**–**7** described in the literature[3–8] (only the *syn*–*syn* conformer of **1** is shown; the *syn*–*anti* conformer is also known). The twisting has been discussed in terms of contributions from the π-electron energy (favouring planarity) and the steric strain energy (opposing planarity).[1,6] The data for compounds **1**–**4** suggest that hydrogen bonding between NH and CO groups stabilises the near-planar forms, and large substituents on nitrogen cause increasingly large dihedral angles. In the compound with the largest dihedral angle in this series, **4**, H-bonding between water molecules and the C=O groups may contribute to the stabilisation of the twisted structure. Very large dihedral angles, 51–89°, have been determined in (*N*,*N*-disubstituted) 1,1-diamino-2,2-dinitroethylenes.[9] Here, too, when NH groups are present, H-bonding with the NO_2 groups stabilises the molecules in nearly planar geometries. Surprisingly, it was reported that semi-empirical calculations (AM1) on model compounds were unable to provide a rationale for the experimentally determined geometries of compounds **1** and **6**: an analogue of **1**, $(HCO)_2C{=}C(NH_2)_2$, was calculated to be stable in the perpendicular form.[6] However, we find that these calculations are not reproducible! Our own AM1 calculations predict this molecule to be nearly planar, as it should be because of hydrogen bonding between the amino and carbonyl groups.

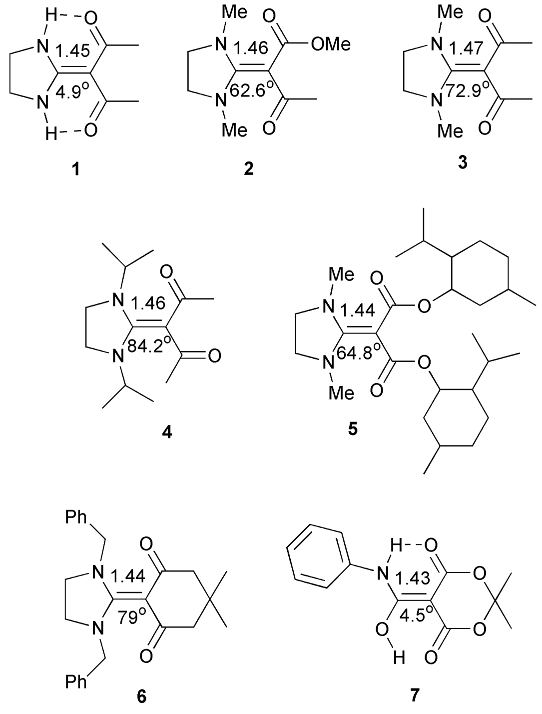

Chart 1 C=C bond lengths in Å and twist angles in degrees.

In the present work we have studied a number of push–pull ethylenes derived from Meldrum's acid (**8**–**19**).[10] The twisting angles have been determined by X-ray crystallography, the zwitterionic character is supported by the ^{13}C-NMR data, and the structures are in general agreement with the results of theoretical calculations. A theoretical analysis of the twisting and rotational barriers in push–pull-substituted model ethylenes of the general formula $(X,Y)C{=}C(CHO)_2$ using density functional theory will be published elsewhere.[11]

Results and discussion

The first hint that compounds **11**–**18** might exists as non-planar zwitterions was provided by the ^{13}C-NMR spectra, which revealed only one carbonyl signal for each compound. Some

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† Electronic supplementary information (ESI) available: tables of X-ray crystallographic bond lengths and angles of compounds **8**–**19** (including selected torsional angles and hydrogen bonds), X-ray crystal structures of compounds **10**, **11**, **13**, **16**, and **18** (Figs. S1–S5) and packing diagrams for **17·H$_2$O** and **19·H$_2$O** (Figs. S6–S7). See http://www.rsc.org/suppdata/p2/b1/b109624a/

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Table 1 Selected ^{13}C-NMR chemical shifts ($CDCl_3$)

Compound	Chemical shifts (ppm) *C*2	2-*Me*	*C*4/6	*C*5	*C*7	N–*Me*	Ar–C_{ipso} or NCH_2	Ar–C_{ortho}	Ar–C_{meta}	Ar–C_{para}	Ar–*Me*	Ar–*Me*
18	101.5	25.6	164.7	67.9	164.9	40.6	137.1	134.0	129.6	134.1	17.8	20.7
17	102.3	26.3	163.4	75.8	164.3	41.7	138.9	122.9	129.5	126.0	—	—
12	103.1	26.4	163.8	86.3	178.1	18.9	137.2	125.3	129.5	128.0	—	—
14	103.1	26.2	164.2	75.8	171.4	62.8	135.0	123.3	129.3	127.0	—	—
8	102.7	26.2	163.7	65.4	166.4	35.7	49.3	—	—	—	—	—
9	103.3	26.3	164.9	71.2	165.4	—	43.2	—	—	—	—	—

selected data are presented in Table 1, and more are found in the Experimental section. Since we usually find two carbonyl signals for unsymmetrically substituted 5-methylene Meldrum's acid derivatives,[12] this suggests that these compounds are either perpendicular olefins or that they have low barriers to rotation about the C=C double bonds. Moreover, the high-field chemical shift of C5 and the low-field shift of C7 are indicative of the zwitterionic structures **20** (Chart 2). Effectively, the signal for C7 moves into the carbonyl region in the 163–178 ppm range. A similar value is reported for the positive carbon atom in other dialkylamino-substituted zwitterions.[13] Chemical shift values similar to those reported in Table 1 and the disappearance of one carbonyl signal is also found in several other, related Meldrum's acid derivatives having NMe_2/arylamino, SMe/arylamino, and OMe/arylamino substituents at C7.[14]

The structures of compounds **8**–**19** were established by X-ray crystallography. The crystal data are collected in Table 2. Representative structures of **8**, **9**, **12**, **14**, **15**, **17**, and **19** are shown in Figs. 1–7, and the remaining structures of **10**, **11**, **13**, **16**, and **18** are given as electronic supplementary information (ESI) (Figs. S1–S5). The lengths of the central C=C bonds and the approximate twisting angles are indicated in Chart 2. Because the Meldrum's acid moieties are not planar, these compounds can in principle have several different angles of twist, with respect to the two carbonyl groups and the two substituents R^1 and R^2 on the C=C bond; the average or the range is given in Chart 2. Tables of bond lengths and angles are available in the ESI.

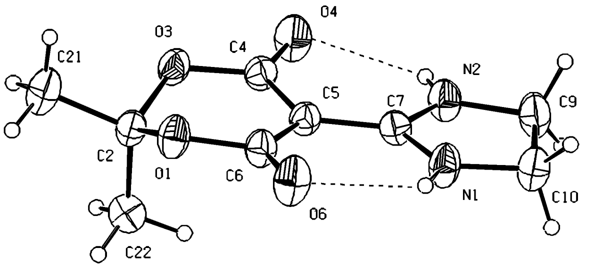

Fig. 1 PLATON drawing of compound **8**.

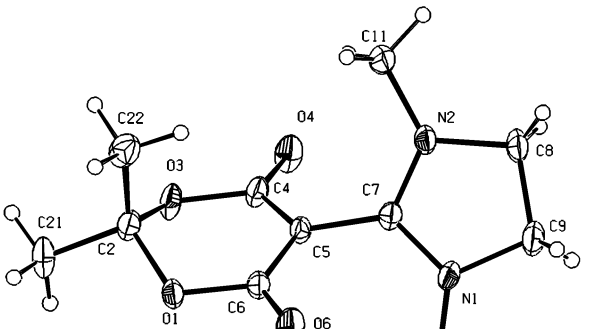

Fig. 2 PLATON drawing of compound **9**.

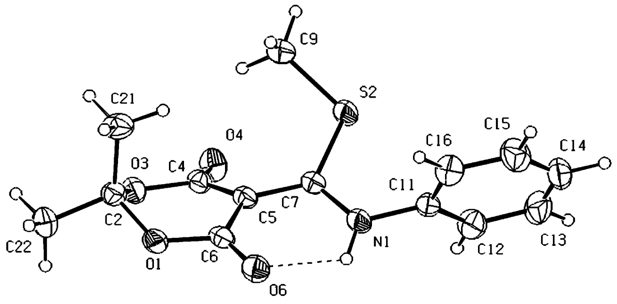

Fig. 3 PLATON drawing of compound **12**.

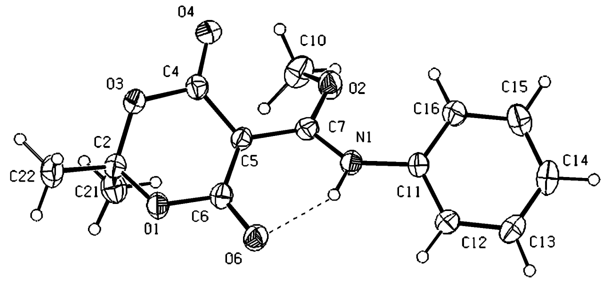

Fig. 4 PLATON drawing of compound **14**.

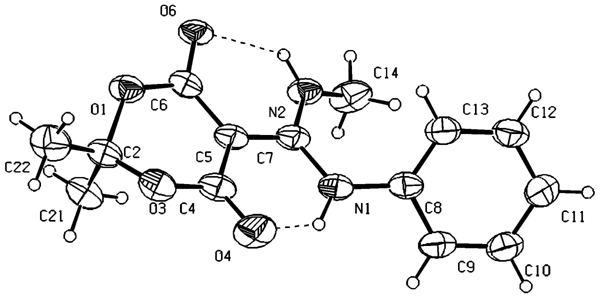

Fig. 5 PLATON drawing of compound **15**.

Inspection of Chart 2 reveals that the central C=C bond lengths are all intermediate between typical single and double bonds (*ca.* 1.54 and 1.34 Å, respectively). The twist angles vary from *ca.* 3° in **8** and **15** to 83° in **19**, and long bonds usually correspond to large twisting angles, although the bond length variation is small and possibly not significant since other factors can contribute to it. There is no such clear correlation between twisting angles and bond lengths in the known compounds listed in Chart 1. It is shown in a density functional theory (DFT) study of model compounds that for small angles of twist, the C=C bond length first decreases due to the breaking of hydrogen bonds; for larger angles of twist the bond length increases.[11]

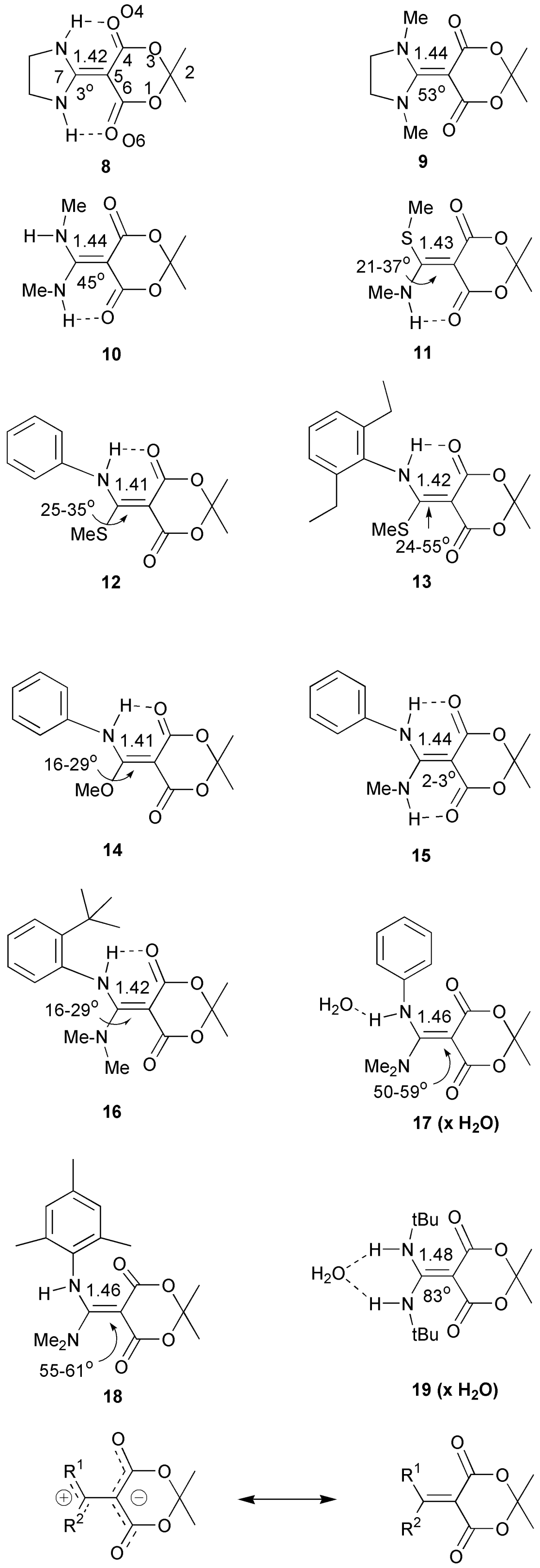

Chart 2 Atom numbering indicated in structure **8**. C=C bond lengths in Å and approximate twist angles in degrees.

The structures of compounds **8**–**19** demonstrate the ability of two amine substituents to induce very large dihedral angles (up to 83°) in accordance with the expectation that better stabilisation of the positive charge in the zwitterion by the two amino groups will lead to a larger degree of twisting. Compounds with MeS and MeO substituents on the double bond usually have dihedral angles around 30° (compare structures **11**, **12**, **13**, and **14** in Chart 2 and Figs. 3, 4 and S2, S3), but these compounds

Table 2 Crystal data

Orthorhombic	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**(17)**·H$_2$O	**(18)**·THF	**(19)**·H$_2$O
Formula	$C_9H_{12}N_2O_4$	$C_{11}H_{16}N_2O_4$	$C_9H_{14}N_2O_4$	$C_9H_{13}NO_4S$	$C_{14}H_{15}NO_4S$	$C_{18}H_{23}NO_4S$	$C_{14}H_{15}NO_5$	$C_{14}H_{16}N_2O_4$	$C_{19}H_{26}N_2O_4$	$C_{15}H_{20}N_2O_5$	$C_{22}H_{32}N_2O_5$	$C_{15}H_{28}N_2O_5$
M	212.21	240.26	214.22	231.26	293.33	349.43	277.27	276.29	346.42	308.33	404.50	316.39
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
a/Å	5.3920(5)	5.365(6)	16.913(5)	5.9086(6)	13.850(4)	10.8985(9)	6.2148(6)	12.328(2)	11.980(1)	8.443(5)	29.65(1)	9.2822(5)
b/Å	9.3030(5)	20.595(8)	6.379(2)	18.381(1)	5.4148(5)	8.451(1)	9.5460(6)	9.1873(9)	11.6629(6)	8.935(5)	12.656(1)	16.716(2)
c/Å	10.441(1)	10.74(1)	19.750(6)	10.460(1)	18.675(7)	19.677(2)	12.059(1)	13.049(3)	13.788(1)	10.454(5)	12.512(5)	11.704(2)
a/°	99.628(6)						96.940(6)					
β/°	94.446(8)	97.69(5)	90.46(2)	104.46(1)	91.85(2)	97.63(1)	99.553(8)	110.21(2)	102.382(9)	97.780(5)	109.44(2)	
γ/°	104.090(6)						105.438(7)					
U/Å^3	496.98(7)	1176(2)	2131(1)	1100.0(2)	1399.8(7)	1796.3(3)	669.7(1)	1387.0(4)	1881.7(2)	781.4(7)	4427(2)	1816.0(4)
T/K	297	297	297	297	297	297	297	297	297	297	297	297
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)^a	$I2/a$ (no 15)^b	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)^a	$P2_1/c$(no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)^a	$P2_1/n$ (no. 14)^a	Pn (no. 7)^c	$C2/c$ (no. 15)	$Cmc2_1$ (no. 36)
Z	2	4	8	4	4	4	2	4	4	2	8	4
μ/m^{-1}	1.13	1.04	1.06	2.88	2.43	2.01	1.05	0.98	0.86	0.99	0.86	0.86
N (R_{int})	1730 (0.0197)	2077 (0.000)	1878 (0.0121)	1925 (0.0175)	2461 (0.0098)	3135 (0.0532)	2317 (0.0254)	2312 (0.0480)	3307 (0.0216)	1487 (0.000)	3885 (0.0132)	984 (0.0219)
Parameters	144	154	145	140	185	221	185	189	231	212	265	142
R (obs. data)	0.0388	0.0779	0.0472	0.0353	0.0374	0.0522	0.0388	0.0509	0.0511	0.0500	0.0813	0.0323
wR_2 (all data)	0.1196	0.2450	0.1295	0.1091	0.1087	0.1624	0.1113	0.1789	0.1635	0.1394	0.2986	0.0925

^{a} Variant of $P2_1/c$. ^{b} Variant of $C2/c$. ^{c} Variant of Pc.

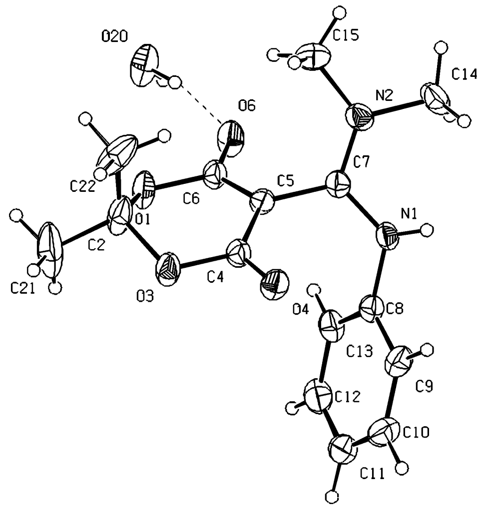

Fig. 6 PLATON drawing of compound **17**.

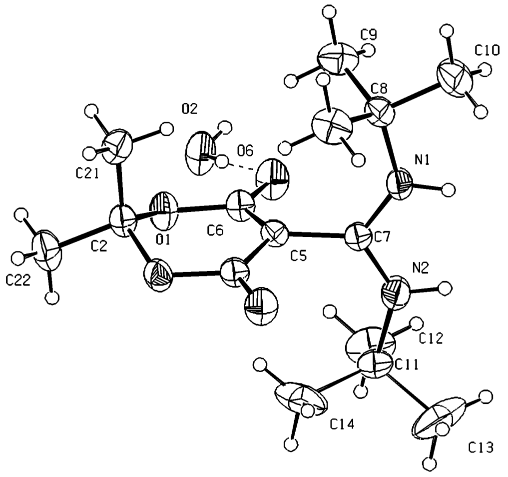

Fig. 7 PLATON drawing of compound **19**.

all have an intramolecular hydrogen bond between an RNH substituent and a carbonyl group of the Meldrum's acid moiety. The presence of such hydrogen bonding works in the opposite direction, favouring planarity. In the *tert*-butylphenylamino compound **16** (Chart 2 and Fig. S4), the NH group is *syn* to a carbonyl group, and consequently the twisting angle is moderate, 16–29° (the tBu group has little effect on the orientation of the phenyl group: the dihedral angle C11–C10–N1–C7 is *ca.* 33°, which is common in this series). When two such hydrogen bonds are present, as in compounds **8** and **15**, almost planar structures are obtained (Figs. 1 and 5). Compounds **17** and **18** have no such H-bonds and thus feature large twist angles of 55–60° (Chart 2 and Figs. 6 and S5). The arylamino-substituted compounds sometimes have the NH *syn* (H-bonded to a carbonyl group) as in **12**, **14**, **15**, and **16**, sometimes *anti* (as in **17** and **18**). The AM1 calculations (see Theory section) reveal that there is a fine balance between the relative energies of the *syn* conformations (having H-bonds) and the *anti* conformations (where H-bonds are absent), and the latter become more favourable when a dielectric field is imposed (ε = 40; Table 3). In the crystal of **17** (Fig. 6), each molecule is H-bonded from the NH group to a molecule of water, thereby obviating any energetic need for an intramolecular H-bond that could have enforced a *syn* conformation. The water molecule is shown in Fig. 6, and it is bonded with the hydrogen atom to a carbonyl group of the Meldrum's acid moiety, and with the oxygen atom to the NH bond of another Meldrum's acid molecule. A packing diagram is shown in the ESI (Fig. S6). However, the presence or absence of water is immaterial for the structures of these molecules: we have solved the X-ray structure of anhydrous **17** as well and determined that the structural parameters are virtually identical with those of the hydrated molecule, but the quality of the anhydrous crystal was poor (*R* ~ 15%). The experimental angle of 55° in **17** is in exact agreement with the AM1-COSMO calculation, and the calculated energy difference between the unsolvated *syn* and *anti* conformations is only 1.6 kcal mol^{-1} (Table 3). In the case of **18** (Fig. S5), the angle of the *anti* conformer is predicted to be 65° (experimental: 60°), and its calculated energy is 3 kcal mol^{-1} above that of the *syn* conformation. The largest angle of twist is found in **19** (83°; Fig. 7), where the two *tert*-butyl groups help to induce orthogonality for steric reasons. A molecule of crystal water is hydrogen bonded to a carbonyl group of the Meldrum's acid moiety (Fig. 7), and at the same time the oxygen atom "ties back" the two N–H bonds on an adjacent molecule (Fig. S7). Because the presence or absence of water does not influence the structure of **17** in the crystal, it is reasonable to assume that the structure of the hydrated **19** also correctly reflects the structure of the *anti–anti* conformer of this molecule in the crystal. The AM1 calculations for **19** (without the solvating water molecule added) show that, for the gas phase, there are two possible *anti–anti* conformations, with dihedral angles of 41 and 93°, but they are 12.0 and 12.4 kcal mol^{-1} above the calculated energy of the *syn–syn* conformer, respectively (Table 3 and Fig. 8). Addition of a dielectric field reduces the energy difference, makes the *syn–anti* conformer the global minimum (twist angle 89°), and places the single *anti–anti* conformer only 3.6 kcal mol^{-1} higher in energy (there is now only one minimum structure; twist angle 94°) (Table 3).

The near-planarity of compound **8** is due to hydrogen bonding between the N–H and C=O groups as shown in Fig. 9. Both intra- and intermolecular H-bonding is present, giving rise to 3-point hydrogen bonds of unequal lengths (2.15 and 2.28–2.29 Å, respectively). The near-planarity of compound **1**, contrasting the high degree of twisting in **2**–**5**, was ascribed to a similar 3-point hydrogen bonding. Three-point intramolecular hydrogen bonding has been reported for 2,6-dibutyramidopyridinium salts (1.97 and 2.03 Å),[15] and both intramolecular (*ca.* 2.15 Å) and intermolecular (*ca.* 2.5 Å) H-bonds were determined for the planar 1,1-diamino-2,2-dinitroethylene.[16] The near-planarity of **15** (Fig. 5), similar to that of **8**, is due to the presence of two intramolecular hydrogen bonds. The calculations for the gas phase (Table 3) come nearest in predicting the small angle of twist (3°). It should be kept in mind, of course, that the calculations ignore crystal packing forces altogether, and hence the excellent overall agreement observed is very remarkable indeed.

Theory

AM1 and DFT calculations

The structures of compounds **8**–**19** as well as several model compounds carrying MeNH groups in place of the arylamino groups were calculated using the semi-empirical AM1 procedure[17] within MOPAC93.[18] The dielectric field simulations were performed with the continuum model COSMO,[19] which is part of the MOPAC package. By placing a molecule in a polarisable continuum, it has the possibility to gain a stabilising energy contribution from the interaction with the dielectric medium. The results are presented in Table 3, where the dihedral angles are the averages of the four possible twisting angles N1–C7–C5–C4, N1–C7–C5–C6, N2–C7–C5–C4, and N2–C7–C5–C6, which are due to the fact that the six-membered ring is not planar. The bond lengths are those of the central C5–C7 bond. The trends are in excellent agreement with the experimentally determined values given in Chart 2. While the calculations for the gas phase (ε = 1) mostly give twist angles

Table 3 AM1 calculations on structures of type **20**[a]

	R^1	R^2	Average dihedral[b]	Bond length[b]	ΔH_f	$\Delta\Delta H_f$
Calculations for the gas phase ($\varepsilon = 1$) *syn* Conformation of NH (hydrogen bond at R^1 and R^2, when possible)						
	MeNH	MeO	4	1.397	−187.8	−5.2
11		MeS	23 (33)	1.402 (1.43)	−148.3	−5.5
10		MeNH	15	1.429	−153.5	−5.4
		Me_2N	28	1.423	−141.5	−3.9
14	PhNH	MeO	19 (22)	1.405 (1.41)	−154.6	−9.7
12		MeS	26 (30)	1.403 (1.41)	−114.8	−8.7
15		MeNH	12 (3)	1.428 (1.44)	−120.3	−9.7
17		Me_2N	28	1.423	−108.1	−7.9
13	$(Et_2Ph)NH$	MeS	27 (39)	1.405 (1.42)	−137.7	−10.2
16	(tBuPh)NH	Me_2N	33 (23)	1.429 (1.42)	−120.6	−6.1
	MesNH	MeO	22	1.407	−175.0	−7.5
		MeS	24	1.405	−135.2	−8.8
		MeNH	12	1.435	−141.6	−10.4
18		Me_2N	37	1.431	−128.9	−7.7
19	tBuNH	tBuNH	18	1.418	−167.3	−3.2
8	Imidazolidine		8 (3)	1.403 (1.42)	−143.9	—
9	*N*,*N*-Dimethylimidazolidine		23 (54)	1.408 (1.44)	−123.7	—
anti Conformation of NH (no hydrogen bond at R^1)						
	MeNH	MeO	25	1.390	−182.6	0
11		MeS	37	1.405	−142.8	0
10		MeNH	33 (46)	1.428 (1.44)	−148.1	0
		Me_2N	44	1.431	−137.6	0
14	PhNH	MeO	26	1.385	−144.9	0
12		MeS	33	1.395	−106.1	0
15		MeNH	25	1.419	−110.6	0
17		Me_2N	40 (55)	1.423 (1.46)	−100.2	0
13	$(Et_2Ph)NH$	MeS	37	1.401	−127.5	0
16	(tBuPh)NH	Me_2N	42	1.426	−114.5	0
	MesNH	MeO	36	1.406	−167.5	0
		MeS	39	1.403	−126.4	0
		MeNH	31	1.423	−131.2	0
18		Me_2N	42 (60)	1.427 (1.46)	−121.2	0
19	tBuNH	tBuNH	30	1.431	−164.1	0
anti–anti Conformation of NH (no hydrogen bond at R^1 or R^2)						
10	MeNH	MeNH	44	1.429	−143.1	5.0
15	PhNH	MeNH	39	1.419	−105.8	4.8
	MesNH	MeNH	44	1.425	−126.7	4.5
19	tBuNH	tBuNH	41	1.424	−155.3	8.8
19[c]	tBuNH	tBuNH	93 (83)	1.456 (1.48)	−154.9	9.2
Calculations for a dielectric field ($\varepsilon = 40$) *syn* Conformation of NH (hydrogen bonds at R^1 and R^2, when possible)						
	MeNH	MeO	4	1.423	−220.1	1.2
11		MeS	37 (34)	1.437 (1.43)	−179.5	−2.7
10		MeNH	29	1.462	−185.8	−1.5
		Me_2N	40	1.462	−174.5	−0.7
14	PhNH	MeO	28 (22)	1.428 (1.41)	−185.8	0.1
12		MeS	38 (30)	1.434 (1.41)	−145.4	−3.7
15		MeNH	25 (3)	1.457 (1.44)	−152.9	−2.8
17		Me_2N	42 (55)	1.458 (1.46)	−141.6	−1.6
13	$(Et_2Ph)NH$	MeS	34 (39)	1.429 (1.42)	−167.2	−4.9
16	(tBuPh)NH	Me_2N	45 (23)	1.459 (1.42)	−153.4	−2.5
	MesNH	MeO	25	1.426	−206.1	−3.9
		MeS	34	1.428	−165.0	−3.5
		MeNH	25	1.460	−174.0	−4.5
18		Me_2N	40	1.459	−162.3	−3.1
19	tBuNH	tBuNH	21	1.449	−194.6	4.1
8	Imidazolidine		6 (3)	1.424 (1.42)	−177.2	—
9	*N*,*N*-Dimethylimidazolidine		35 (54)	1.437 (1.44)	−157.3	—
anti Conformation of NH (no hydrogen bond at R^1)						
	MeNH	MeO	31	1.435	−221.3	0
11		MeS	53	1.442	−176.8	0
10		MeNH	44 (46)	1.462 (1.44)	−184.3	0
		Me_2N	60	1.465	−173.8	0
14	PhNH	MeO	27	1.430	−185.9	0
12		MeS	56	1.442	−141.7	0

Table 3 (*Contd.*)

	R^1	R^2	Average dihedral[b]	Bond length[b]	ΔH_f	$\Delta\Delta H_f$
15		MeNH	36	1.456	−150.1	0
17		Me_2N	57	1.462	−140.0	0
13	$(Et_2Ph)NH$	MeS	55	1.441	−162.3	0
16	(tBuPh)NH	Me_2N	63	1.465	−150.9	0
	MesNH	MeO	53	1.439	−202.2	0
		MeS	57	1.443	−161.5	0
		MeNH	46	1.460	−169.5	0
18		Me_2N	65 (80)	1.466 (1.46)	−159.2	0
19	tBuNH	tBuNH	89	1.478	−198.7	0
	anti–anti Conformation of NH (no hydrogen bond at R^1 or R^2)					
10	MeNH	MeNH	60	1.466	−182.0	2.3
15	PhNH	MeNH	51	1.460	−148.2	1.9
	MesNH	MeNH	64	1.467	−167.6	1.9
19	tBuNH	tBuNH	94 (83)	1.472 (1.48)	−195.1	3.6

[a] The average calculated dihedral angles about the central C5=C7 bond and the length (Å) of that bond are given. [b] Experimental values are given in brackets. [c] There are two minima for *anti–anti* conformations in the gas phase; see text and Fig. 8.

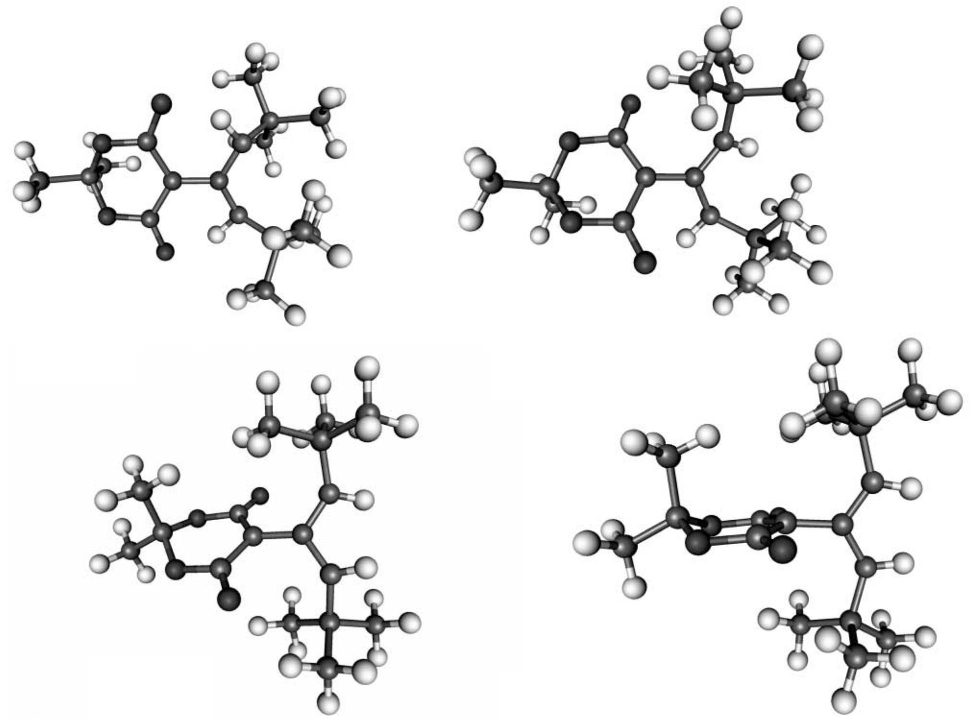

Fig. 8 Calculated conformations of **19** in the gas phase (clockwise from top left: *syn–syn*, *syn–anti*, and the two *anti–anti* structures) (B3LYP/6-31G*).

that are too small (except for **15**, *vide supra*), the inclusion of a dielectric field ($\varepsilon = 40$) greatly improves the agreement with the experimental values, so that almost perfect correlation is obtained. We have shown elsewhere that it is necessary to include a dielectric field with dielectric constants ε up to 40 in the calculations when dealing with zwitterionic or mesoionic compounds, for example, in B3LYP/6-31G* calculations of energies and IR spectra.[20]

The sequence of twist angles in the order R_2N > MeS > MeO roughly follows the experimentally observed and expected abilities of the substituents to stabilise a positive charge in the zwitterion (**20**). The additional entries in Table 3, included in order to increase the number of substituent combinations, confirm this observed trend. It should be noted, however, that there are several examples in the literature of alkoxy groups giving rise to larger twisting angles than RS groups, thus giving rise to

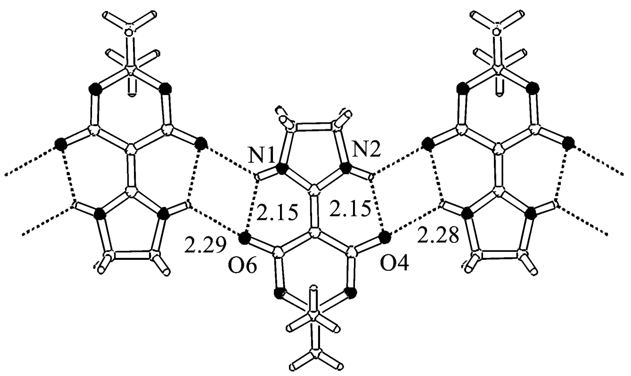

Fig. 9 3-Point hydrogen bonding pattern in compound **8** drawn in PLUTON.

Table 4 Rotational barriers relative to the *syn* conformers ($\Delta\Delta H_f$/kcal mol^{-1}) for structures of type **20** (AM1 calculations)

			Gas phase ($\varepsilon = 1$)		COSMO ($\varepsilon = 40$)	
	R^1	R^2	ΔH_f (TS)	$\Delta\Delta H_f$	ΔH_f (TS)	$\Delta\Delta H_f$
	MeNH	MeO	−175.7	12.1	−217.1	3.0
11		MeS	−135.7	12.6	177.6	1.9
10		MeNH	−138.2	15.3	−182.7	3.1
		Me_2N	−130.1	11.5	−172.3	2.2
14	PhNH	MeO	−141.0	13.6	−182.8	3.0
12		MeS	−101.8	13.0	−143.2	2.2
15		MeNH	−105.3	15.0	−149.2	3.7
17		Me_2N	−97.6	10.5	−139.0	2.6
13	$(Et_2Ph)NH$	MeS	−126.0	11.7	−163.8	3.4
16	(tBuPh)NH	Me_2N	−112.5	8.1	−150.4	3.0
	MesNH	MeO	−162.9	12.1	−201.8	4.3
		MeS	−123.7	11.5	−162.3	2.7
		MeNH	−127.8	13.8	−169.4	4.6
18		Me_2N	−119.9	9.0	−158.5	3.8
19	tBuNH	tBuNH	−149.2	18.1	−188.1	6.5
8	Imidazolidine		−123.5	20.4	−169.8	7.4
9	*N*,*N*-Dimethylimidazolidine		−114.9	8.8	−155.1	2.2

Table 5 B3LYP/6-31G*-calculated energies (in kcal mol^{-1}) of the conformers of **19** (*cf.* Fig. 8)

	Gas phase ($\varepsilon = 0$)			Dielectric field ($\varepsilon = 40$)		
	Dihedral angle/deg	Bond length/Å	$\Delta\Delta H_f$	Dihedral angle/deg	Bond length/Å	$\Delta\Delta H_f$
syn–syn	0	1.444	0	4	1.449	0
syn–anti	35	1.435	4.8	40	1.440	2.0
anti–anti	42	1.427	11.0	43	1.439	5.2
anti–anti	86	1.472	14.5	84	1.477	−0.7

the suggestion that oxygen is better than sulfur at stabilising a positive charge.[1a]

Rotational barriers were also estimated using the AM1 method (Table 4). It is known that this method tends to underestimate these barriers in the gas phase by *ca.* 10 kcal mol^{-1}.[21] In the present study, they are of the order 9–20 kcal mol^{-1}, *i.e.* small enough to provide for rapid rotation about the C=C double bonds at room temperature, as required by the ^{13}C NMR data. Moreover, the barriers decrease dramatically in a dielectric field ($\varepsilon = 40$) due to a much more effective stabilisation of the zwitterionic transition state.[22] Although the absolute values of these barriers may not be quantitatively correct, they nevertheless imply that even those molecules that are nearly planar due to the stabilising intramolecular hydrogen bonds will undergo rapid rotation about the central C5–C7 bonds at room temperature. The rotational barriers are the subject of a detailed DFT study of model compounds.[11]

Additional DFT calculations[23] on **19** were performed at the B3LYP/6-31G* level of theory,[24] and four conformers were located as energy minima (Fig. 8) in the gas phase as well as in a simulated dielectric continuum. *In vacuo*, the *syn–syn* structure with an average dihedral angle of 3° is the global minimum in agreement with the AM1 calculations. The *anti–syn* conformer has a significantly larger twist (37°) and lies 4.8 kcal mol^{-1} higher in energy. As the X-ray structure possesses a "tied-back" *anti–anti* conformation, these conformers are of particular interest. Two were located, being 11–14 kcal mol^{-1} less stable than the minimum structure, one with an average dihedral angle of 42°, and the other nearly perpendicular. The latter structure possesses a much longer central C–C bond (1.472 Å), compared to 1.427 Å in the former and agrees very well with the X-ray structure of **19** (Chart 2 and Fig. 7). The calculated energy difference between these latter two gas-phase *anti–anti* conformers is small enough to allow the conclusion that other effects, such as the dipolar environment, intermolecular hydrogen bonds, and crystal packing forces, may be sufficient to make the orthogonal structure more stable.

The inclusion of a dielectric field model (PCM, $\varepsilon = 40$)[25] in the calculations changes the situation drastically. There still exist the four minimum structures (Fig. 8), but in contrast to the gas-phase calculations, the most stable conformer is now the orthogonal *anti–anti* structure, 0.7 kcal mol^{-1} lower in energy than the *syn–syn* conformer (Table 5). Despite the relatively small energy difference, the necessity of including polarity effects is clearly seen: this converts the least stable gas-phase conformer into the preferred structure in a polar medium, in agreement with the experimental X-ray data for compound **19** (Chart 2 and Fig. 7).

Conclusion

Push–pull stabilised ethylenes such as compounds **1**–**19** exist in highly zwitterionic forms (see **20**) which approach 90° twist angles about the central C=C bond (C5–C7), especially when sterically demanding substituents are present. Near-planarity is achieved only when two stabilising intramolecular hydrogen bonds are present (as in **1**, **8**, and **15**). Semiempirical AM1 calculations with the inclusion of a dielectric field (ε = 40)[20] provide excellent agreement with experimental X-ray structures. It is predicted that all these molecules, even those that are formally planar due to hydrogen bonding, undergo rapid rotation about the central C=C bonds at or near room temperature. DFT-SCRF calculations confirm an orthogonal structure as the most stable conformer of **19** in a polar medium.

Experimental

General

NMR spectra were recorded on a Bruker AX 200 spectrometer (200.13 MHz for ^1H and 50.34 MHz for ^{13}C) with $SiMe_4$ as internal standard. *J* values are given in Hz.

Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four circle diffractometer employing graphite monochromated Mo-Kα radiation (0.71073 Å). The structures were solved by direct methods (SHELXS86)[26] and refined using the teXsan package.[27] Non-hydrogen atoms were refined with anisotropic displacement factors while hydrogen atoms were included at calculated positions except for compound **12**, where the hydrogen atoms were located and refined with isotropic thermal parameters. The atomic nomenclature is defined in the figures, which are drawn with PLATON,[28] and packing diagrams were produced with PLUTON.[29] All calculations were performed with the WINGX package.[30] The crystal data are collected in Table 2.

CCDC reference numbers 177773–177784. See http://www.rsc.org/suppdata/p2/b1/b109624a/ for crystallographic files in .cif or other electronic format.

Materials

Compound **17** was prepared according to ref. 31, compound **12** according to ref. 32, compound **14** according to ref. 33 and compounds **10**, **11** and **19** according to ref. 34.

5-(Imidazolidin-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione 8. To 5-[bis(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione[35] (2.48 g; 10 mmol) in 30 ml of methylene chloride was added ethylenediamine (0.88 g; 10 mmol), and the mixture was stirred for 3 h. The solution was evaporated *in vacuo* and the resulting solid recrystallised from acetone to yield 1.78 g (84%) of pale yellow crystals, mp 188–190 °C; δ_H ($CDCl_3$) 1.63 (s, 6H), 3.76 (s, 4H), 8.22 (br s, 2H); δ_C ($CDCl_3$) 26.3, 43.2, 71.2. 103.3, 164.9, 165.4; IR (KBr) ν_{max} 3044, 2999, 1701, 1604, 1404, 1291, 1266, 1189, 1103, 931, 793 cm^{-1}. HRMS *m/z* 212.0796; calcd for $C_9H_{12}N_2O_4$ 212.0797.

5-[(*N*,*N'*-Dimethylimidazolidin-2-ylidene)]-2,2-dimethyl-1,3-dioxane-4,6-dione 9. To 5-[bis(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (2.48 g; 10 mmol) in 30 ml of methylene chloride was added *N*,*N'*-dimethylethylenediamine (0.88 g; 10 mmol), and the mixture was stirred for 3 h. The solution was evaporated *in vacuo* and the resulting solid recrystallised from acetone to yield 1.79 g (74%) of pale yellow crystals, mp 218–220 °C; δ_H ($CDCl_3$) 1.72 (s, 6H), 3.04 (s, 6H), 3.82 (s, 4H); δ_C ($CDCl_3$) 26.2, 35.7, 49.3, 65.4, 102.7, 163.7, 166.4; IR (KBr) ν_{max} 2992, 1702, 1652, 1559, 1419, 1401, 1375, 1326, 1296, 1262, 1203, 1177, 1052, 978, 924 cm^{-1}. Found: C, 54.95; H, 6.74; N, 11.45. $C_{11}H_{16}N_2O_4$ requires: C, 54.97; H, 6.72; N, 11.66%.

5-[(2,6-Diethylanilino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 13. A solution consisting of 14.4 g (100 mmol) of isopropylidene malonate (Meldrum's acid) and 28 ml of triethylamine (200 mmol) in 70 ml of dry acetonitrile was stirred for 30 min, then 19.1 g of 2,6-diethylphenyl isothiocyanate were added, and the mixture was heated at 60 °C for 12 h. A total of 7.0 ml (100 mmol) of iodomethane was added dropwise to the above mixture at room temperature, and the resulting solution was then stirred for 48 h. The solution was concentrated under reduced pressure, and 5 ml of *n*-hexane was added to precipitate yellow crystals which were collected by filtration and recrystallised from hot THF to give 21 g (60%) of pale yellow crystals, mp 150–151 °C; IR (KBr) ν_{max} 2970, 2832, 1686, 1631, 1526, 1470, 1350, 1018, 950, 915, 796, 694 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.19 (t, ^3J = 7.6 Hz, 6H, CH_3CH_2–), 1.75 (s, 6H, CMe_2), 2.35 (s, 3H, SCH_3), 2.49–2.62 (m, 4H, CH_3CH_2–), 7.17 (d, ^3J = 7.9 Hz, 2H), 7.31 (t, ^3J = 7.6 Hz, 1H), 12.2 (s, br, 1H, NH); δ_C (100 MHz, $CDCl_3$) 14.2 (CH_3CH_2–), 18.3 (SCH_3), 24.6 (CH_3CH_2–), 26.2 (CMe_2), 84.1 (C=*C*–CO), 102.9 (*C*Me_2), 126.6, 129.3, 134.0, 140.8, 163.9 (*C*=C–CO), 180.1 (CO). Anal. calcd. for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01. Found: C, 61.78; H, 6.69; N, 3.96%.

5-[(Methylamino)(phenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 15. To a solution of 5-[(methylthio)(phenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione[36] (0.51 g; 1.7 mmol) in 10 ml of THF was added 10 ml of 40% aqueous methylamine solution. The mixture was stirred overnight, the solvent removed *in vacuo*, and the product was recrystallised from THF/hexane to yield 0.41 g (86%) of white crystals, δ_H ($CDCl_3$) 1.89 (s, 6H), 2.73 (d, 3H), 7.42 (m, 5H); δ_C ($CDCl_3$) 26.1, 32.4, 74.6, 102.5, 124.8, 126.5, 129.2, 137.6, 162.3, 166.6; IR (KBr) ν_{max} 3440, 2993, 1654, 1600, 1390, 1377, 1264, 1208, 1119, 930 cm^{-1}. Found: C, 60.93; H, 6.01; N, 9.99. $C_{14}H_{16}N_2O_4$ requires: C, 60.86; H, 5.84; N, 10.14%.

5-[(2-*tert*-Butylanilino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione. This compound was prepared as a precursor to **16**. A solution consisting of 10 g (40 mmol) of 5-[bis(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione and 7.5 g (50 mmol) in 50 ml of dry acetonitrile was refluxed for 30 h. The resulting solution was concentrated under reduced pressure, then 5 ml of *n*-hexane were added to precipitate white crystals, which were collected by filtration and recrystallised from hot THF to give 9.1 g (yield 65%) as a colourless solid, mp 148–149 °C; IR (KBr) ν_{max}3449, 1717, 1655, 1544, 1386, 1374, 1265, 1207, 1146, 1019, 943, 798, 768 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.40 (s, 9H, *t*-Bu), 1.78 (s, 6H, CMe_2), 2.32 (s, 3H, SCH_3), 7.18 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1H), 7.22–7.26 (m, 1H),7.33 (td, ^3J = 7.3, ^4J = 1.4 Hz, 1H), 7.50 (dd, ^3J = 8.1, ^4J = 1.5 Hz), 12.8 (s, br, 1H, NH); δ_C (100 MHz, $CDCl_3$) 18.3 (SCH_3), 26.1 (CMe_2), 30.3 (CMe_3), 34.9 (*C*Me_3), 85.2 (C=*C*–CO), 102.7 (*C*Me_2), 126.7, 127.5, 128.9, 129.2, 135.2, 144.8, 163.8 (*C*=C–CO), 178.3 (CO). Anal. calcd. for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01. Found: C, 61.62; H, 6.64; N, 4.04%.

5-[(2-*tert*-Butylanilino)(dimethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione16. 5-[(2-*tert*-Butylanilino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (12.2 g, 35 mmol) was dissolved in 50 ml THF (previously dried over sodium). A stream of gaseous dimethylamine was bubbled *via* a pipette through the stirred solution at such a slow rate that the gas is just absorbed. The solution was then heated at 50° C for 24 h in a closed, round-bottom flask. The resulting solution was concentrated by evaporating some of the solvent to precipitate white crystals which were collected by filtration and recrystallised from a hot THF to give 9.1 g (75%) as colourless crystals, mp 117–118 °C.

IR (KBr) ν_{max} 3440, 1698, 1654, 1582, 1540, 1457, 1394, 1265, 1200, 1062, 930, 799 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.42 (s, 9H, *t*-Bu), 1.74 (s, 6H, CMe_2), 2.79 (s, 6H, NMe_2), 6.88 (dd, ^3J = 7.5,^4J = 1.8 Hz, 1H), 7.14–7.22 (m, 2H), 7.44 (dd, ^3J = 7.5,^4J = 1.8 Hz, 1H), 10.2 (s, br, 1H, NH); δ_C (100 MHz,$CDCl_3$) 26.2 (CMe_2), 30.3 (CMe_3), 35.1 (*C*Me_3), 41.7 (NMe_2), 76.5 (C=*C*–CO), 102.0 (*C*Me_2), 124.3, 126.4, 126.9, 127.7, 137.1, 142.5, 162.8 (CO), 164.7 (*C*=C–CO). Anal. calcd. for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 65.70; H, 7.50; N, 8.01%.

5-[(Mesitylamino)(methylthio)]methylene-2,2-dimethyl-1,3-dioxane-4,6-dione. This compound was prepared as a precursor to compound **18**. A mixture of 5-[bis(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (2.48 g; 10 mmol), 2,4,6-trimethylaniline (2.70 g; 20 mmol) and 30 ml of acetonitrile was refluxed for 6 h and then stirred for a further 48 h at rt. The resulting solution was evaporated *in vacuo* to yield a yellow oil. This oil was dissolved in 5 ml of ethanol and allowed to stand overnight to produce white crystals, which were collected by filtration and recrystallised from ethanol to yield 2.38 g (71%) of colourless crystals, mp 163–164 °C; δ_H ($CDCl_3$) 1.74 (s, 6H), 2.16 (s, 6H), 2.28 (s, 3H), 2.32 (s, 3H), 6.91 (s, 2H), 12.05 (br s, 1H); δ_C ($CDCl_3$) 18.0, 18.2, 21.0, 26.2, 84.1, 102.8, 129.2, 132.7, 134.7, 138.8, 163.8, 180.1; IR (KBr) ν_{max} 3444, 1712, 1659, 1550, 1400, 1376, 1270, 1208, 1022, 926, 791, 719, 696 cm^{-1}; MS *m*/*z* 335 (36), 320 (57), 305 (12), 277 (38), 230 (100), 185 (55), 158 (20), 142 (10), 119 (18), 91 (18), 77 (12), 43 (18). Found: C, 61.02; H, 6.52; N, 4.12. $C_{17}H_{21}NO_4S$ requires: C, 60.87; H, 6.32; N, 4.18%.

5-[(Mesitylamino)(dimethylamino)]methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 18. To a solution of 5-[(mesitylamino)-(methylthio)]methylene-2,2-dimethyl-1,3-dioxane-4,6-dione (335 mg; 1.0 mmol) in 15 ml of THF were added 2 ml of dimethylamine solution (40% w/v in water) followed by HgO (216 mg, 1.0 mmol). The mixture was stirred overnight and filtered. The filtrate was evaporated *in vacuo* and the resulting crystals recrystallised from THF to yield 164 mg (49%) of colourless crystals, mp 226–228 °C; δ_H (CDCl$_3$) 1.73 (s, 6H), 2.14 (s, 6H), 2.80 (s, 6H), 6.88 (s, 2H), 9.19 (br s, 1H); δ_C (CDCl$_3$) 17.8, 20.3, 25.6, 40.6, 67.9, 101.5, 129.6, 134.02, 134.06, 137.1, 164.7, 164.9; IR (KBr) ν_{max} 3448, 2985, 1690, 1655, 1627, 1582, 1479, 1445, 1389, 1375, 1355, 1261, 1066, 928 cm^{-1}; MS *m*/*z* 332 (3%), 317 (7), 387 (11), 274 (36), 256 (11), 230 (31), 185 (100), 172 (13), 158 (43), 142 (17), 119 (23), 91 (28), 77 (21), 58 (20), 43 (72); HRMS *m*/*z* 332.1733; $C_{18}H_{24}N_2O_4$ requires 332.1733.

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