DE GRUYTER Pure Appl. Chem. 2016; 88(4): 317–331

Conference paper

Amélie Wannebroucq, Andrew P. Jarmyn, Mateusz B. Pitak, Simon J. Coles and John D. Wallis*

Reactions and interactions between *peri*-groups in 1-dimethylamino-naphthalene salts: an example of a "through space" amide

DOI 10.1515/pac-2015-1103

Abstract: 8-Dimethylaminonaphthalene-1-carbaldehyde reacts readily at 0 °C with benzoyl or pivaloyl chloride by O-acylation and formation of a N–C bond (1.566(2)–1.568(3) Å) between the *peri*-substituents to give a salt. The reaction is promoted by electron donation from the dimethylamino group to the carbonyl group, akin to the properties of an amide. In contrast, the corresponding methyl ester and N,N-diisopropylamide react with acid in ether by protonation of the dimethylamino group and formation of a hydrogen bond to the carbonyl group, while under similar conditions the N,N-dimethylamide undergoes ready hydrolysis to the acid. The structures of products are determined by X-ray crystallography, and from the latter hydrolysis crystals containing zwitterionic 1-dimethylammonium-naphthalene-8-carboxylate and the corresponding O-protonated cation along with dimethylammonium and triflate ions were obtained.

Keywords: acylation; aldehydes; ESOC-19; hydrogen bonding; intramolecular reactivity.

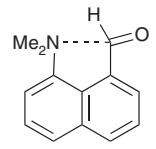
Introduction

The *peri*-disubstituted naphthalene framework has been used to study interactions between pairs of nucleophilic and electrophilic groups placed at the *peri* positions since the groups are held near to one another and usually are not involved in conjugation with the aromatic ring [1–6]. Thus, a dimethylamino group is particularly sensitive to the nature of its electrophilic neighbour, whereas a methoxy group is much less sensitive due to its lower nucleophilicity [7]. Interactions of a dimethylamino group with an aldehyde, ketone, ester or amide group in **1–6** [1–3, 8–10] as well as various electrophilic alkenes such as **7–8** have been investigated by X-ray crystallography [11]. N···C separations lie in the range 2.764–2.413 Å, well within van der Waals separation. There is a small pyramidalisation of the carbonyl carbon towards the dimethylamino group,

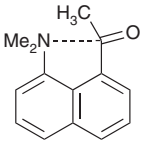
Article note: A collection of invited papers based on presentations at the 19th European Symposium on Organic Chemistry (ESOC-19), Lisbon, Portugal, 12–16 July 2015.

***Corresponding author: John D. Wallis,** School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK, e-mail: john.wallis@ntu.ac.uk. http://orcid.org/0000-0001-7259-8783
Amélie Wannebroucq and Andrew P. Jarmyn: School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK. http://orcid.org/0000-0002-3687-424X (A. Wannebroucq); http://orcid.org/0000-0000-0000-0000 (A.P. Jarmyn)
Mateusz B. Pitak and Simon J. Coles: UK National Crystallography Service, University of Southampton, Highfield Campus, Southampton, SO17 1BJ, UK. http://orcid.org/0000-0002-3680-7100 (M.B. Pitak); http://orcid.org/0000-0001-8414-9272 (S.J. Coles)

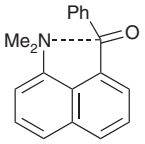
indicative of a n–π^* interaction between the groups, which can be considered as an early stage in bond formation between the groups. However, in the case of even more electrophilic alkenes a long covalent bond is formed between the groups (1.612–1.654 Å) resulting in zwitterionic structures as in compounds such as **9–10** [11–13]. Together with compounds such as clivorine **11** which contain *trans*-annular interactions between amine and carbonyl groups with N···C distances in the range 1.99–2.29 Å, this provides a series for the study of the formation of the C–N bond [14, 15].



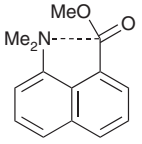
1



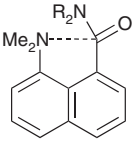
2



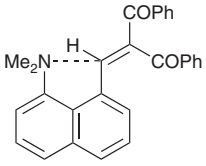
3



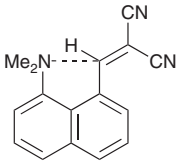
4



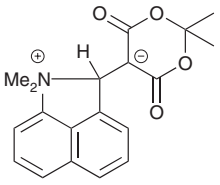
5 R= Me
6 R = *i*-Pr



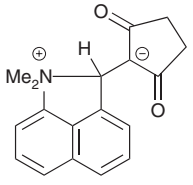
7



8

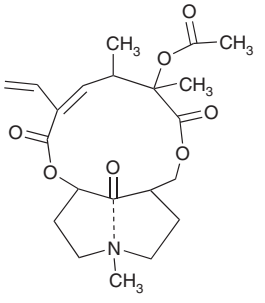


9



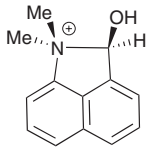
10

For the cases where no substantial bond formation between *peri* groups has taken place, the nucleophilic dimethylamino group may still modify the reactivity of its neighbour. Indeed, we have reported that treatment of the *peri*-aldehyde **1** with acid in ether at 0 °C leads to immediate protonation on the aldehyde oxygen atom, with concomitant formation of a bond between the *peri* substituents to give **12** [13]. We have observed similar results for the protonation of the corresponding methyl, isopropyl and trifluoromethyl ketones under similar conditions to give salts **13–15** with C–N bonds in the range 1.637–1.670 Å [9]. In contrast, the *t*-butyl and phenyl ketones prefer to protonate on nitrogen to give **16** and **17** with a hydrogen bond from N–H to the pi surface of the carbonyl group. We report here studies on the reaction of aldehyde **1** with further

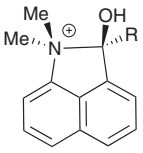


11

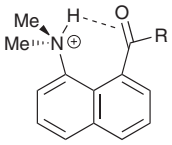
electrophiles and in particular the structures of its adducts with benzoyl chloride and pivaloyl chloride. In addition, we report the results from protonation of the ester **4** and amides **5** and **6** which were undertaken to establish whether they protonated on the dimethylamino or carbonyl group.



12



13 R = CH_3
14 R = *i*-Pr
15 R = CF_3

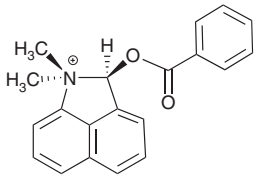


16 R = *t*-Bu
17 R = Ph

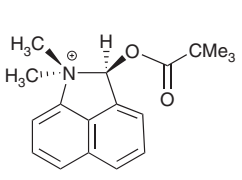
Results and discussion

Acylation of aldehyde 1

Reaction of the aldehyde **1** with benzoyl chloride in dry ether at 0 °C gave immediately a white solid, whose ^{1}H and ^{13}C NMR spectra support its assignment as the chloride salt of cation **18** in which the aldehyde oxygen has been benzoylated and the *peri*-dimethylamino group has added to the carbonyl group. The methine group created by addition to the aldehyde group has NMR resonances at δ_H: 8.06 and δ_C: 100.9 ppm, and the two N-methyl groups have distinct resonances at δ_H: 3.89 and 4.29 and δ_C: 49.3 and 56.6 ppm. The carbonyl group's stretch is typical for an ester at 1732 cm^{-1}. Reaction of aldehyde **1** with pivaloyl chloride gave the corresponding chloride salt of cation **19**, with methine resonances at δ_H: 7.59 and δ_C: 100.4 ppm, and a carbonyl stretch at 1749 cm^{-1}. Reactions with acetyl chloride or t-butyldimethylsilyl triflate gave the corresponding products which rapidly hydrolysed to give cation **12**. This is unusual chemistry, and is similar to the chemistry of a carboxylic amide except that the *peri*-dimethylamino group provide the extra electron density needed in the carbonyl group "through space" rather than "through bond". In contrast to aldehyde **1,** the closely related phenyl ketone **3** did not react with benzoyl chloride under the same conditions or even in THF at 60 °C, indicative of the lower reactivity of an aryl ketone to the adjacent dimethylamino group.



18



19

To characterise the bond formed between the two *peri*-groups, crystals of the chloride salts of cations **18** and **19** were grown by evaporation of acetonitrile solutions and their structures determined by X-ray crystallography at 150 K. The crystal structure of both salts are triclinic in space group $P\bar{1}$. The structure of cations **18** and **19** are shown in Fig. 1, with selected geometric details in Table 1. The new N–C bond between the *peri* groups is 1.568(3) Å long in cation **18** and 1.566(2) Å in cation **19**. The single C–O bond, which arose from addition to the carbonyl group, is 1.424(3) Å long in **18** and 1.417(2) Å in **19**. The N–CH_3 bonds at the positively charged N group are considerably longer (1.507(3)–1.514(2) Å) than in aldehyde **1** (1.468(6)–1.470(6) Å) [8] where the N atom is uncharged. The geometry of the ester groups are typical for such groups [16]. Thus the aldehyde **1** reacts like a "through space amide", with the dimethylamino nitrogen lone pair donating electron density into the carbonyl's π^* orbital "through space" to activate the group to O-acylation, just as is seen in the corresponding reaction with acid to give cation **12**.

The crystal packing arrangements of the chloride salts are shown in Fig. 2. In both cases the chloride ion makes five short contacts to hydrogen atoms in the range 2.65–2.79 Å: to the naphthyl hydrogen *ortho* to the positively charged nitrogen atom (2.66–2.67 Å), to three N-methyl hydrogens and to the sp^3 methine hydrogen.

For cation **12** in the O-protonated salts of aldehyde **1**, the N–C bond between the *peri* groups lies in the range 1.624(4)–1.638(2) Å and the C–O(H) bond lies in the range 1.352(4)–1.362(4) Å, considerably longer (by *ca* 0.06 Å) and shorter (by *ca* 0.06 Å), respectively than the corresponding bonds in cations **18** and **19**. This

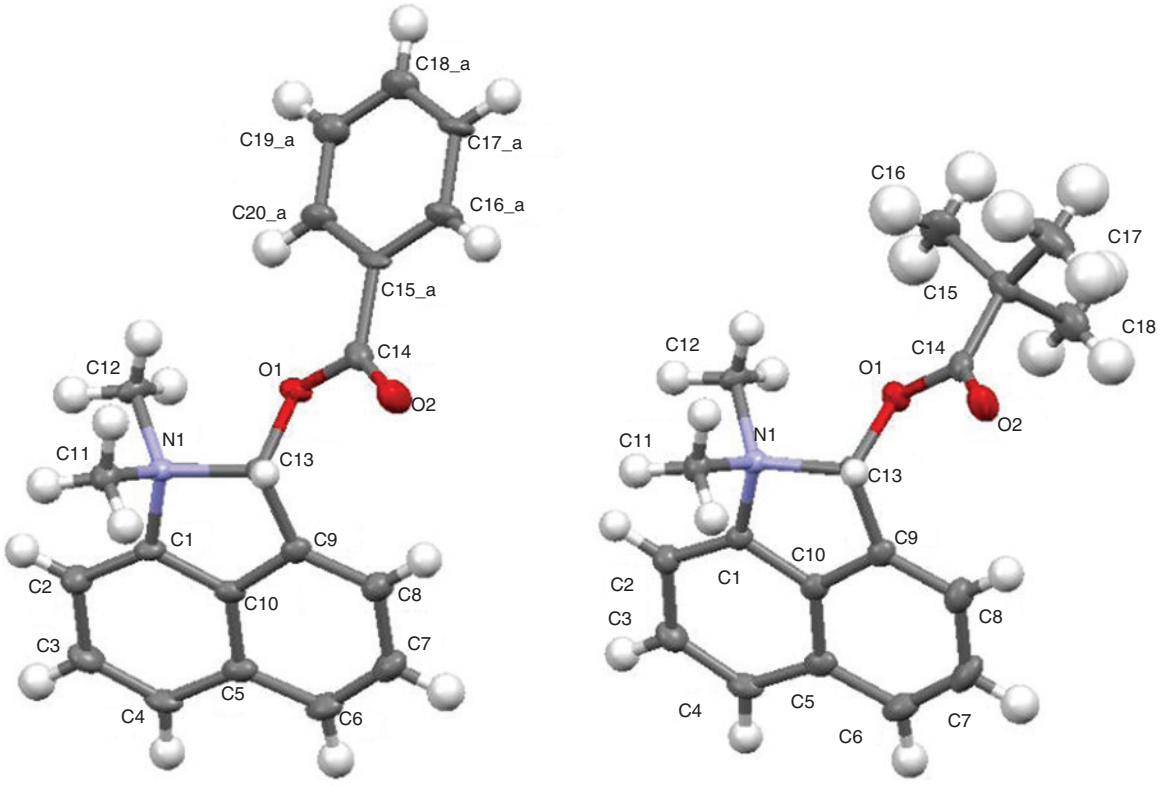
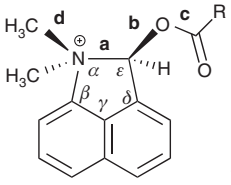


Fig. 1: Molecular structures of the cations **18** and **19** with atomic displacement parameters drawn at the 50 % level. For **18**, only one position of the disordered phenyl group is shown.

Table 1: Selected geometric details of cations **18** and **19**.



τ = torsion angles: H_3C–N–C–O(C=O)

	a/Å	b/Å	c/Å	d/Å	τ/°
18	1.568(3)	1.424(3)	1.363(3)	1.507(3)	1.3(2)
				1.509(3)	−120.06(18)
19	1.566(2)	1.417(3)	1.373(2)	1.512(2)	4.1(2)
				1.514(2)	−124.9(2)
	α/°	**β/°**	**γ/°**	**δ/°**	**ε/°**
18	105.29(16)	108.50(18)	113.4(2)	108.72(19)	104.07(17)
19	105.31(12)	108.89(15)	112.89(17)	108.93(15)	103.92(14)

difference can be explained in terms of the orientations of the oxygen lone pairs with respect to the C–N bond between the *peri* groups (Fig. 3). Thus, in the cation of the protonated material one of the hydroxyl oxygen atom's lone pairs is aligned with the lobe of the antibonding orbital of the N–C bond between *peri* groups lying out beyond the carbon atom, and thus lengthening the bond. In the acylated salts the two lone pairs of the alkoxy oxygen, irrespective of whether they are considered to be two sp^3 lone pairs or one sp^2 and one p lone pair, do not overlap with the C–N anti-bonding orbital since the (Me_2)N–C–O–C(=O) torsion angles are 145.97(18) and 146.22 (14)° in contrast to 75(2)° for the corresponding (Me_2)N–C–O–H torsion angle for the

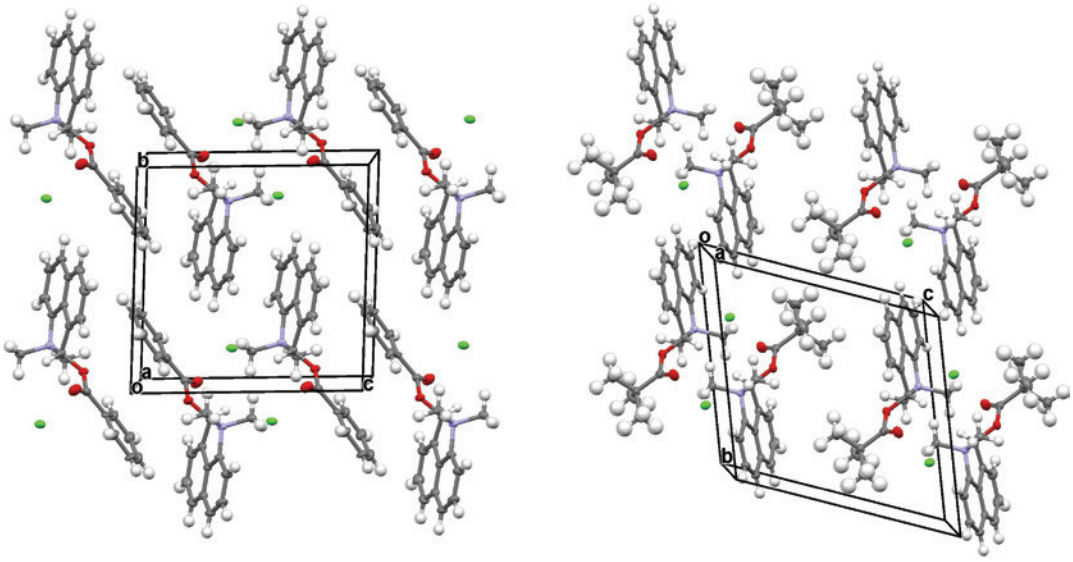


Fig. 2: Crystal packing arrangements for **18**.Cl (left) and **19**.Cl (right).

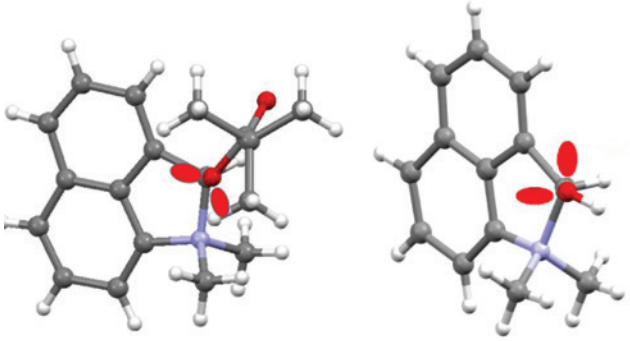


Fig. 3: Comparison of the relative orientation of the O-substituent with respect to the C–N bond between *peri*-substituents in cation **19** (left) and cation **12** (right).

protonated salt. In solution, away from the constraint of crystal packing on molecular conformations, the situation may of course be different.

Thus, the close approach of a dimethylamino group to the aldehyde group in **1** activates the carbonyl group to reaction with electrophiles, either protons or acyl groups. Such n–pi* interactions between an oxygen and a carbonyl group have been identified as important in stabilising the conformations of small molecules e.g. interactions with ester carbonyl groups in aspirin and N-acyl proline esters [17, 18], and also the conformations of proteins via interactions between amides [19, 20]. These interactions, while not forming a covalent bond, do modify the properties of the two groups [21].

Protonation of a *peri*-ester 4 and *peri*-amides 5 and 6

Following the discovery that protonation of naphthalenes bearing *peri*-related dimethylamino and ketone groups leads to either O-protonation with bond formation between the *peri* groups for methyl, isopropyl and trifluoromethyl ketones or, for larger ketone substituents such a *t*-butyl and phenyl, to N-protonation and hydrogen bond formation with the *peri* group [9], we decided to examine the crystal structures of protonated products where the ketone group is replaced by the less electrophilic ester or amide group. The methyl ester **4** and the N,N-dimethyl- and N,N-diisopropylamides **5** and **6** were prepared by *peri*-lithiation of 1-dimethylaminonaphthalene and reaction with methyl chloroformate or the corresponding N,N-dialkylcarbamoyl

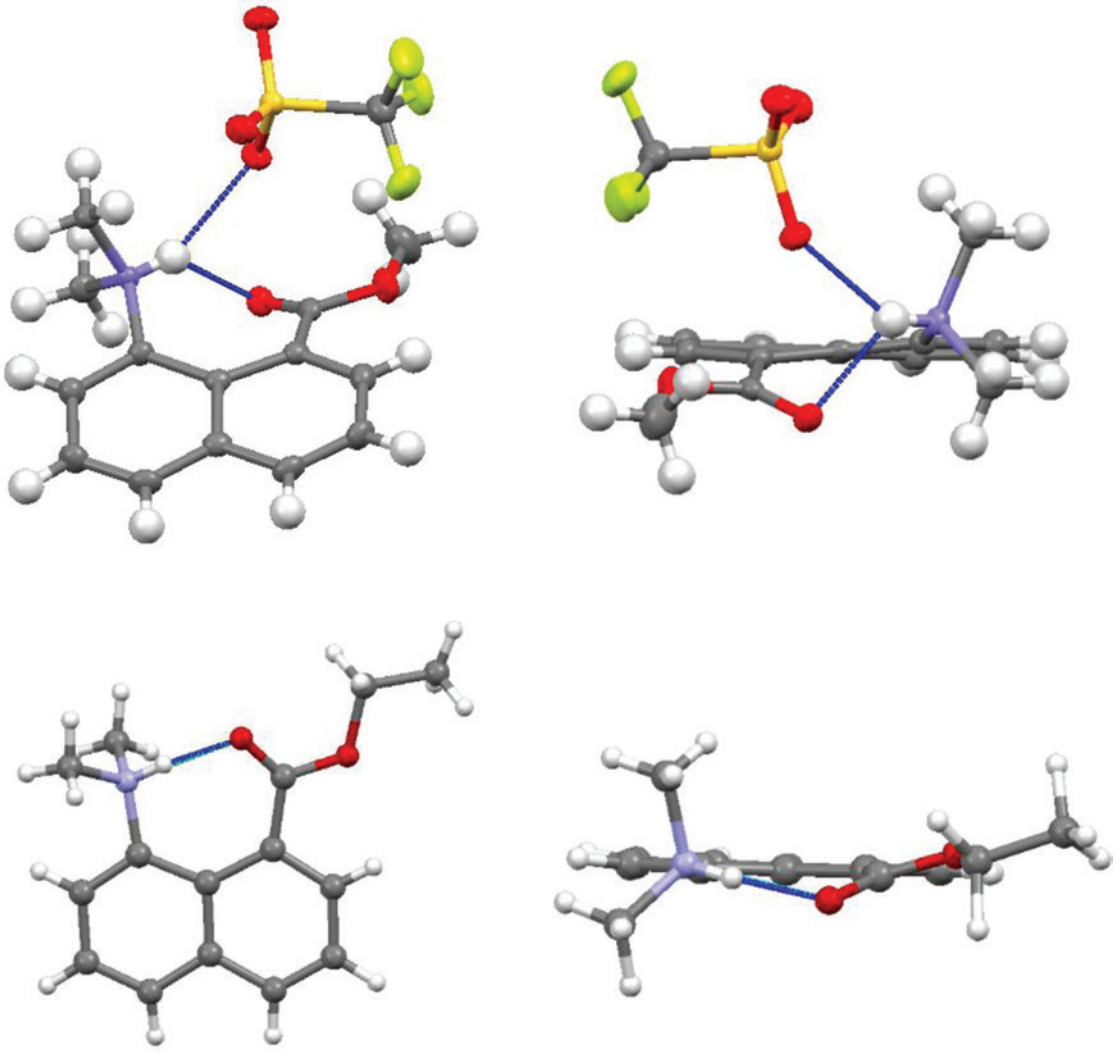


Fig. 4: Molecular structure of the N-protonated cation in **4-H**.triflate (top) and in **4-H**.picrate [22] (bottom).

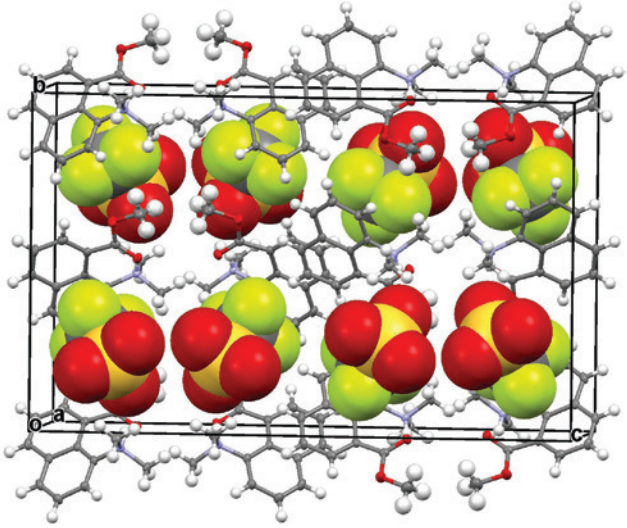
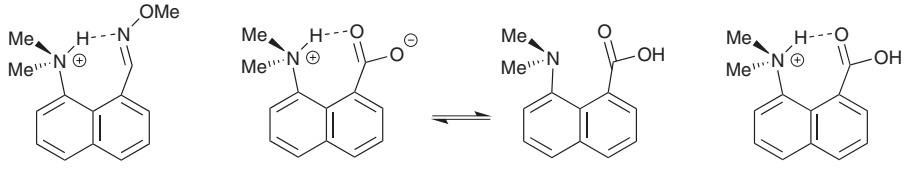


Fig. 5: Crystal packing arrangement of **4-H**.triflate salt, with triflate ions shown in space-filling mode.

chloride. Compounds **4–6** were reacted with triflic acid in ether to precipitate salts from which crystals were grown by evaporation of appropriate solutions.

The crystal structure of the triflate salt of ester **4** is orthorhombic in space group *Pbca*. The structure of the cation is shown in Fig. 4 and the crystal packing arrangement in Fig. 5. The structure shows that protonation has taken place on the nitrogen atom, with formation of two rather long hydrogen bonds: one to the ester carbonyl group (2.06(4) Å) and one to a triflate anion (2.23(3) Å). Geometric details of the hydrogen bonding is given Table 2. The *peri* groups are splayed apart in the naphthalene plane by 4.2 and 3.1° for the dimethylammonium and ester groups respectively, as well as being strongly displaced to opposite sides of the aromatic plane to facilitate the formation of the hydrogen bond to the triflate ion. The hydrogen bond to the ester carbonyl group makes an angle of 95.3(9)° with the carbonyl bond and the (Ar)C–C=O···H torsion is 52(1)°. The naphthalene system is strongly twisted to displace the *peri*-substituents to opposite sides of the aromatic plane, in contrast to the situation for the N-protonated cations of the bulky phenyl and t-butyl ketones, **16** and **17** (Table 2). The ester carbonyl stretch occurs at 1686 cm^{-1} in the infra-red spectrum.

The room temperature ^1H NMR of a $CDCl_3$ solution of this salt shows a strongly deshielded ^1H resonance for the N–H group at δ_H: 13.00 ppm, and there is just one signal for the dimethylamino group in both the ^1H and ^{13}C NMR spectra. In solution, there is no requirement for the second hydrogen bond to a triflate ion, so there may just be a tight intramolecular hydrogen bond to the ester group lying close to the aromatic plane. Previously, Schuster et al. reported the NMR spectra of the tetrafluoroborate salt of cation **4-H**$^+$ in nitrobenzene [23] and the crystal structure of the picrate salt of the corresponding ethyl ester [22]. In this latter case the anion is not involved in hydrogen bonding with the protonated dimethylamino group, and consequently, the hydrogen bond between *peri* groups is much shorter (1.70 Å) and the structure is also much less twisted with the *peri* N and C substituent atoms lying close to the naphthalene plane, and the angle at hydrogen much closer to linear (174° *cf.* 128°) and a lower torsion angle about the carbonyl group ((Ar)C–C=O···H: 29° v 52°) (Table 2). Similar hydrogen bonding between *peri* groups has been observed in the crystal structures of oxime **20** [24] and carboxylic acid **21** [1]. For the latter, there are two crystallographically unique molecules, one of which exists as a zwitterion with an intramolecular hydrogen bond **21** and the other as the uncharged amino acid **22**.



20 **21** **22** **23**

The X-ray crystal structure determination of the triflate salt of diisopropylamide **6** at 100 K showed that the crystal system was monoclinic and the space group $P2_1/c$. The structure of the cation is shown in Fig. 6 and the crystal packing in Fig. 7. Protonation has taken place at the dimethylamino group and there is an intramolecular hydrogen bond to the oxygen atom of the *peri*-amide group. In contrast to the ester **4**, there is no additional hydrogen bond from the protonated dimethylamino group to a triflate anion. The amide group, unlike the ester group in **4**, is rotated out of the naphthalene plane by 57.6° due to the steric interaction of the isopropyl groups with the *ortho* hydrogen atom so that the hydrogen bond lies to one side of the naphthalene plane, in contrast to the ester salt. The hydrogen bond is much shorter than in the ester cation **4-H**+ (1.60(2) *cf.* 2.06(4) Å) and is close to linear at hydrogen, unlike in the ester salt. However, the angle the hydrogen bond makes with the carbonyl group (97.6(7)°) and the (Ar)C–C=O···H torsion angle (56.5(7)°) are similar to those in the triflate salt of ester **4** (Table 2). The hydrogen bond does not lie in the plane of the carbonyl group, nor perpendicular to it, but at an intermediate position. The *peri* groups are splayed apart in the aromatic plane, more notably at the amide group. The hydrogen bonding has affected the amide carbonyl group which is longer than in an unprotonated amide (1.2595(17) *cf.* 1.23 Å). Solution ^1H NMR shows a strongly deshielded NH resonance, and two sets of N–Me and N-isopropyl signals, and in the infra-red spectrum the carbonyl frequency has moved from 1618 to 1574 cm^{-1} on salt formation.

Table 2: Hydrogen bonding geometries in salts of **4**, **6** and related compounds.

Compound	O···H/Å	N–H/Å	C=O/Å	O···H–N /°	H···O=C /°	(Ar)C–C=O···H /°	Δ(H, O) /Å	splaying of *peri*-bonds (N, C)/°
4-H.triflate[a]	2.06(4)	0.84(3)	1.209(3)	128(3)	95.3(9)	52(1)	−0.46(3), 1.094(4)	−4.2, 3.1
4-H.picrate [18][b]	1.70	0.86	1.214(3)	174	105.3	29.4	0.14, 0.457	−2.5, 6.0
6-H.triflate	1.60(2)	0.99(2)	1.2595(17)	170(2)	97.6(7)	56.5(7)	0.51(2), 0.690(2)	−1.8, 4.7
17.BF_4	1.80(3)	0.92(3)	1.229(3)	156(2)	98.6(8)	56.5(9)	0.56(3), 0.949(3)	−0.8, 5.9
21.23.Me_2NH_2(triflate)$_2$[c]	1.65(3)	0.91(3)	1.253(3)[c]	170(3)	102(1)	42(1)	0.31(3), 0.640(3)	−1.5, 7.1
	1.53(3)	0.96(3)	1.244(3)[c]	177(3)	110(1)	2(1)	0.04(3), 0.222(3)	−2.8, 7.3
23.triflate[d]	1.83(2)	0.85(2)	1.215(2)	145(2)	105.7(3)	32.0	0.35(2), −0.641(2)	−4.4, 5.3

[a]and a hydrogen bond from N–H to triflate anion: 2.23(3) Å, angle at H 146(3)°.

[b]the hydrogen positions were not refined.

[c]and two hydrogen bonds from Me_2NH_2 to two triflates, 1.95(1) Å, angle at H 157(3)° and 2.00(1) Å, angle at H 151(2)°. The *peri*-naphthalene molecule is disordered 1:1 between containing a carboxylate and a carboxylic acid group.

[d]and a hydrogen bond from CO_2H to triflate, 1.83(3) Å, angle at H 171(3)°.

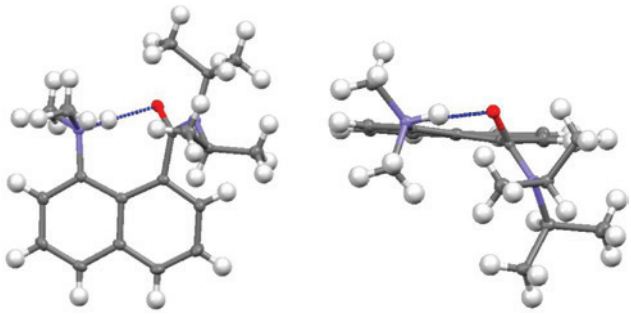


Fig. 6: Molecular structure of N-protonated cation **6-H⁺**.

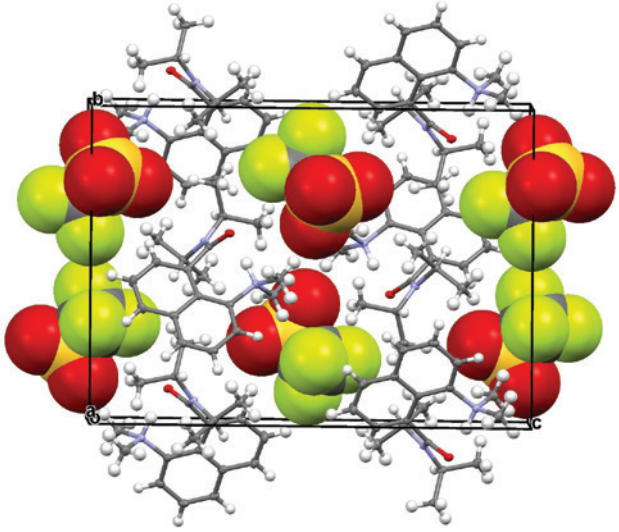


Fig. 7: Crystal packing arrangement for **6-H**.triflate, with triflate ions shown in space-filling mode.

Reaction of the N,N-dimethylamide **5** with triflic acid gave a white oily solid which on standing for a day followed by trituration with ether gave a white solid whose NMR was consistent with a mixture of the triflate salts of 1-dimethylaminonaphthalene-8-carboxylic acid **21** and dimethylamine. Thus, the amide group has been hydrolysed by atmospheric water to form the corresponding carboxylic acid. Crystals were grown from acetonitrile and studied by X-ray diffraction at 100 K. The crystal structure is monoclinic in space group $P2_1/c$ and is composed of a 1:1:1 ratio of the zwitterionic 1-dimethylammonio-naphthalene-8-carboxylate **21**, its O-protonated cation **23** and a dimethylammonium cation along with two triflates. The zwitterion is hydrogen bonded to its O-protonated salt via the carboxylate oxygen, and the two species are arranged across a centre of inversion with a 1:1 disorder in the location of the labile hydrogen atom (Fig. 8). There are two such pairs which are crystallographically unique, and the unit cell contains two of each of these pairs accompanied by eight triflate anions and four dimethylammonium cations (Fig. 9).

The two crystallographically unique *peri*-naphthalene species each contain an internal hydrogen bond between *peri* groups and in one case the carboxylic group has rotated about 34° out of the naphthalene plane while it is close to the naphthalene plane in the other. This leads to a difference in the lengths of the intramolecular hydrogen bond: 1.65(3) and 1.53(3) Å, respectively. These almost linear hydrogen bonds makes angles of 102(1) and 110(1)° with the carboxyl bond, while the (Ar)C–C=O···H torsion angles are 42(1) and 2(1)°. So the hydrogen bonding arrangements are quite different, though the splaying apart of the substituents are similar with the carboxyl group splayed out further, so that for the case where the carboxyl group is nearly coplanar with the naphthalene there is a close O···H contact with the *ortho*-H of 2.20 Å. The second carboxyl oxygen is involved in the intermolecular hydrogen bonding to the carboxyl group of another *peri*-naphthalene. In the

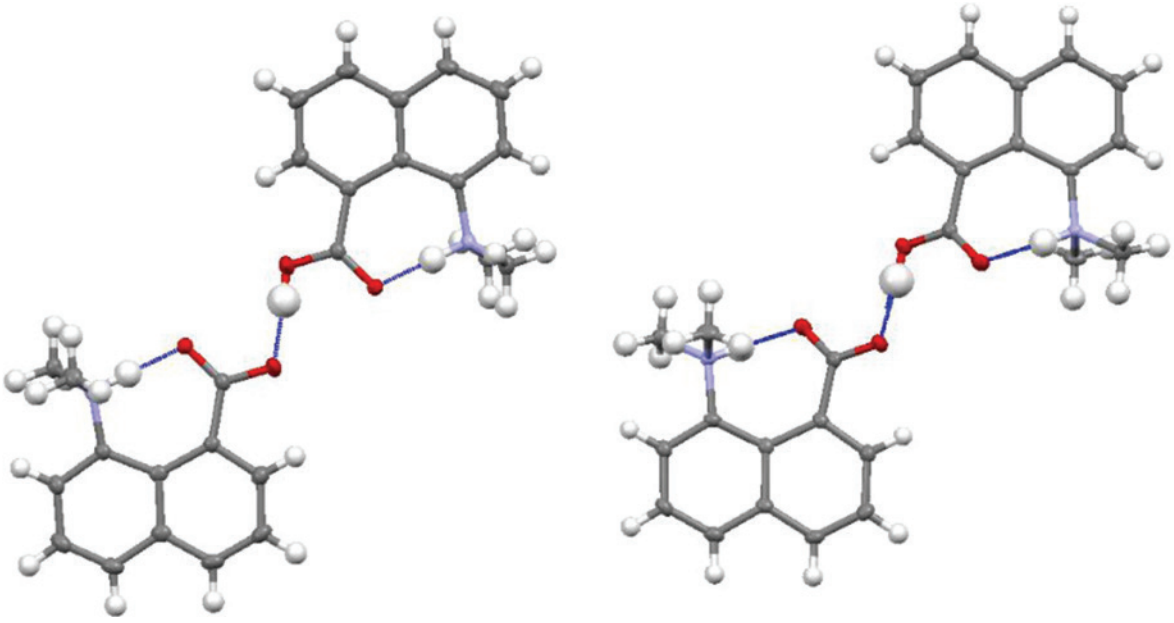


Fig. 8: The two crystallographically unique molecules of 8-dimethylammonium-naphthalene-1-carboxylate, each hydrogen bonded to a molecule of its O-protonated salt. The zwitterion and conjugate acid are related by a centre of inversion, and the central hydrogen atom is disordered across this centre, with just one position shown. The angle between the carboxyl group and the aromatic plane is 5.0° (left) and 34.3° (right), and the former has the shorter intramolecular N-H···O hydrogen bond (1.53(3) v 1.65(3) Å).

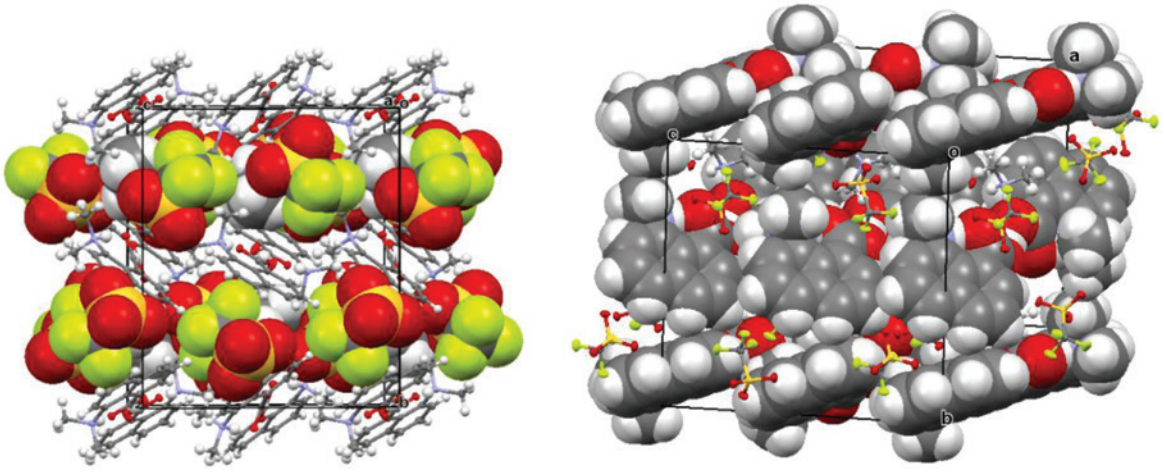


Fig. 9: Crystal packing arrangement for **21.23**.Me_2NH_2.$(triflate)_2$ viewed down the *a* axis showing alternating layers of **21**/**23** species (ball and stick mode) and Me_2NH_2/triflate anions (space filling mode) perpendicular to the *b* axis (left) and (b) view showing the orientation of the naphthalene species (space filling mode) (right).

two unique carboxy groups the carbon-oxygen bond which is intramolecularly hydrogen bonded is shorter (1.253(3) and 1.244(3) Å) than the bond involved in the intermolecular hydrogen bonding (1.277(3) and 1.275(3) Å). The dimethylammonium cation is hydrogen bonded to two independent triflate ions. The crystal structure contains alternate planes composed of the *peri*-naphthalene species and then the triflate and dimethylammonium ions.

Interestingly, slow evaporation of a $CDCl_3$ solution of the triflate salt of ester **4**, led to growth of a large crystal of the triflate of the corresponding protonated carboxylic acid **23**. The crystal structure of the acid salt is triclinic in space group *P*$\bar{1}$ and shown in Fig. 10. The compound is protonated on the dimethylamino

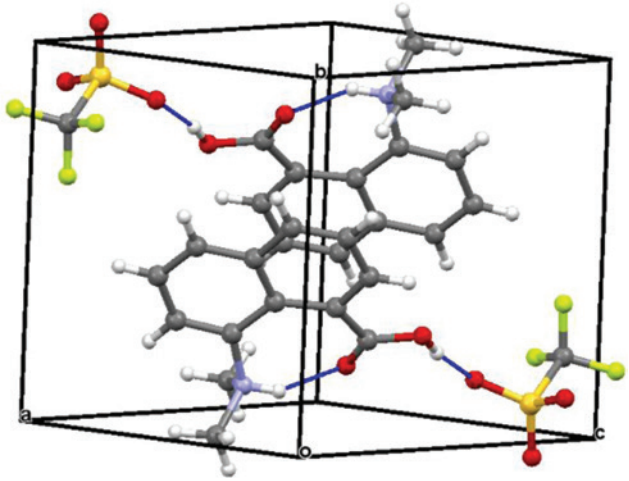


Fig. 10: Crystal structure of **23**.triflate showing hydrogen bonding interactions.

group which forms an intramolecular hydrogen bond to the carbonyl of the carboxylic acid group. The –OH of the carboxylic acid is hydrogen bonded to a triflate anion (Table 2). Together with the ready hydrolysis on protonation of the amide **5**, it suggests a catalytic role for the hydrogen to which the ester and amide carbonyl groups make a hydrogen bond.

Conclusion

Aldehyde **1** is readily acylated due to the interaction of the adjacent nitrogen lone pair with the carbonyl group through space which acts to increase the electron density on the oxygen, showing how a neighbouring group can modify reactivity. Similar such interactions between oxygen and carbonyl groups have been proposed to be stabilising features in molecular conformations [17–20]. Although aldehyde **1** and some *peri*-ketones react with acid in a similar way, the corresponding methyl ester **4** and N,N-diisopropylamine **6** protonate on nitrogen with formation of an intramolecular hydrogen bond. This may be due to the lower reactivity of the functional group to nucleophiles, since the alternative structure derived by addition to the carbonyl group and O-protonation would not be particularly sterically hindered for ester **4**, though the *peri*-bond formed could be weakened by anomeric effects from two oxygens. Additional structures of the corresponding N-protonated carboxylic acid and carboxylate have also been determined. In most cases described here the hydrogen bond is linear at hydrogen and the bond angle between the hydrogen bond and the carbonyl bond lies in the range 95–110°. However, the direction of approach of hydrogen to the oxygen varies from in the carbonyl plane, and thus near to the sp^2 lone pair, to *ca* 50° to the carbonyl plane and thus nearer to the pi electron density. It is interesting to note the proposal that hydrogen bonding to the pi surface of a carbonyl group promotes the kinetics of deprotonation *alpha* to the carbonyl group in various enzyme active sites [25]. Future work will look at the effect of hydrogen bonding on the rate of hydrolysis of the ester or amide group.

Experimental

General

Solution NMR spectra were measured on a JEOL ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.5 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard at 24 °C unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on

a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling unless otherwise stated, and are reported in cm^{-1}. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. Ester **4** and amides **5** and **6** were prepared by *peri*-lithiation of 1-dimethylaminonaphthalene and treatment with methyl chloroformate, N,N-dimethylcarbamoyl chloride or N,N-diisopropylcarbamoyl chloride [26, 27].

Preparation of 2-benzoyloxy-1,1-dimethyl-1,2-dihydrobenzo[cd]indol-1-ium chloride, 18.Cl

A stirred solution of aldehyde **1** (0.10 g, 0.50 mmol) in dry ether (5 mL) under nitrogen was treated with a 1M solution of benzoyl chloride in dry ether (0.625 mL, 0.625 mmol) at room temperature to give a white precipitate. After stirring for 10 min. the solid was filtered and washed with dry ether to give a **18.Cl** as a white solid (0.14 g, 82 %), m.p. 125–127 °C (dec.), δ_H (400 MHz, $CDCl_3$): 9.12 (1H, d, J = 7.3 Hz, Ar-H_1), 8.13 (2H, dd, J = 8.4, 1.1 Hz, *ortho*-Ph-H_2), 8.12 (1H, d, J = 8.2 Hz, Ar-H_1), 8.06 (1H, s, 2-*H*), 8.04 (1H, d, J = 8.2 Hz, Ar-H_1), 7.78–7.88 (3H, m, Ar-H_3), 7.74 (1H, d*t*, J = 7.6, 1.1 Hz, *para*-Ph-H_1), 7.55 (2H, t, J = 7.8 Hz, *meta*-Ph-H_2), 4.29 (3H, s, N-CH_3), 3.89 (3H, s, N-CH_3); δ_C (100.5 MHz, $CDCl_3$): 164.8 (*C*=O), 145.1, 135.6, 130.9, 130.6, 130.1, 129.9, 129.2, 128.1, 127.6, 127.3, 127.0, 125.9, 122.9, 117.7 (Ar-C_{16}), 100.9 (2-*C*), 56.6 (N-*C*H_3), 49.3 (N-*C*H_3); ν_{max}: 3023, 2995, 2953, 1732, 1643, 1603, 1584, 1503, 1471, 1451, 1409, 1371, 1348, 1315, 1264, 1242, 1175, 1099, 1086, 1066, 1034, 1023, 1008, 968, 920, 897, 830, 812, 793, 768, 709, 692, 677 cm^{-1}; found: C: 70.62, H: 5.29 N: 4.23 %; $C_{20}H_{18}NO_2Cl$ requires C: 70.69, H: 5.34, N: 4.12 %.

Preparation of 1,1-dimethyl-1,2-dihydro-2-(2′,2′-dimethyl)propanoyloxy-benzo[cd] indol-1-ium chloride 19.Cl

A stirred solution of aldehyde **1** (0.10 g, 0.50 mmol) in dry ether (5 mL) under nitrogen was treated with a 1M solution of trimethylacetyl chloride in dry ether (0.625 mL, 0.625 mmol) at room temperature to give a white precipitate. After stirring for 30 min. the solid was filtered and washed with dry ether to give **19.Cl** as a white powder (0.15 g, 94 %), m.p. 168–172 dec °C. δ_H (400 MHz, $CDCl_3$) 9.13 (1H, d, J = 7.2 Hz, Ar-H_1), 8.05 (1H, d, J = 8.2 Hz, Ar-H_1), 7.98 (1H, d, J = 8.2 Hz, Ar-H_1), 7.77–7.86 (2H, m, Ar-H_2), 7.60 (1H, d, J = 7.5 Hz, Ar-H_1), 7.59 (1H, s, 2-*H*), 4.24 (3H, s, N-CH_3), 3.88 (3H, s, N-CH_3), 1.34 (9H, s, C(CH_3)$_3$; δ_C (100.5 MHz, $CDCl_3$) 176.8 (*C*=O), 145.2, 131.0, 130.2, 129.9, 128.0, 127.7, 127.4, 127.0, 122.3, 118.2 (Ar-C_{10}), 100.4 (2-*C*H), 56.6 (N-*C*H_3), 49.6 (N-*C*H_3), 39.5 (*C*(Me)$_3$), 26.8 (3 × *C*H_3). ν_{max}: 3022, 2970, 1749, 1505, 1470, 1396, 1275, 1118, 1093, 1049, 1009, 972, 941, 905, 847, 829, 810, 767, 749 cm^{-1}; found: C: 67.53, H: 7.01, N: 4.32 %; $C_{18}H_{22}N\,O_2Cl$ requires C: 67.60, H: 6.93, N: 4.38 %.

1-Dimethylammonio-8-methoxycarbonylnaphthalene triflate, 4-H$^+$.$CF_3SO_3^-$

A stirred solution of methyl 8-dimethylaminonaphthalene-1-carboxylate (0.50 g, 1.84 mmol) in dry ether (20 mL) under nitrogen was treated with a few drops of triflic acid, and stirred for 1 h. The solvent was evaporated under vacuum, and the residue left at 5 °C. After 72 h the product had solidified and was collected and washed with ether to give the product, **4-**H.triflate, as a pink powder, m.p. 103–104 °C dec.; δ_H (400 MHz, $CDCl_3$): 13.00 (1H, br, N-*H*), 8.73 (1H, d, J = 7.4 Hz, Ar-H_1), 8.33 (1H, d, J = 7.6 Hz, Ar-H_1), 8.25 (1H, d, J = 8.0 Hz, Ar-H_1), 8.10 (1H, d, J = 8.0 Hz, Ar-H_1), 7.80 (1H, t, J = 7.9 Hz, Ar-H_1), 7.68 (1H, t, J = 7.9 Hz, Ar-H_1), 4.16 (3H, s, O-CH_3), 3.46 (6H, s, N-(CH_3)$_2$); δ_C (100.5 MHz, $CDCl_3$): 172.0 (*C*=O), 138.1, 137.4, 137.2, 136.0, 133.3, 127.2, 126.0, 123.8, 123.0, 122.9 (Ar-C_{10}), 120.7 (q, J = 321 Hz, *C*$F_3SO_3^-$), 54.9 (O-*C*H_3), 47.8 (N-(*C*H_3)$_2$); ν_{max}: 3159, 3074, 2963, 1686, 1516, 1463, 1431, 1224, 1215, 1205, 1172, 1145, 1092, 1025, 993, 870, 840, 797, 784, 762, 751, 635, 574, 516, 501 cm^{-1}; found C: 47.46, H: 4.13, N: 3.53 %; $C_{14}H_{16}NO_2.CF_3SO_3$ requires: C: 47.49, H: 4.25, N: 3.69 %.

Slow evaporation of the NMR sample led to the growth of a large crystal of 8-dimethylammonio-naphthalene-1-carboxylic acid triflate, **23**.triflate, m.p. 155–157 °C, ν_{max}: 2988 br, 1681, 1624, 1602, 1519, 1466, 1418, 1290, 1219, 1198, 1155, 1027, 876, 839, 780, 768, 722, 634, 626, 586, 572 cm^{-1}.

Reaction of N,N-dimethylamide 5 with triflic acid

A solution of N,N-dimethylamide **5** (0.20 g, 0.82 mmol) in dry ether (4 mL) was treated with a solution of triflic acid (0.124 g, 0.83 mmol) in dry ether (2 mL) under nitrogen to give an oily precipitate. After stirring for 2 h. and then standing for 24 h. the precipitate remained oily. The ether was allowed to evaporate in the air, and the residue left to stand for a further 24 h. Addition of dry ether, stirring and scratching with a glass rod gave a solid which was collected, washed with dry ether and dried (0.187 g) identified as a 1:1.2 mixture of 1-dimethylammonio-naphthalene-8-carboxylate triflate and dimethylammonium triflate. δ_H (400 MHz, CD_3CN): 8.76 (1H, dd, J = 7.2, 1.4 Hz, Ar-H_1), 8.25 (1H, dd, J = 7.6, 1.4 Hz, Ar-H_1), 8.12 (1H, J = 7.3 Hz, Ar-H_1), 7.98 (1H, d, J = 7.3 Ar-H_1), 7.65–7.71 (2H, m, Ar-H_2), 6.99 (1.2 × 2H, br t, J(^{14}N, ^{1}H) = 44.6 Hz, NH_2), 3.14 (6H, s, N(CH_3)$_2$), 2.64 (1.2 × 6H, t, J = 5.5 Hz, $NH_2(CH_3)_2$); δ_C (100.5 MHz, (CD_3CN): 174.4 (*C*=O), 141.2, 137.5, 137.0, 136.7, 133.0, 128.0, 127.3, 126.9, 125.5, 123.5 (Ar-H_{10}), 118.7 (q, J = 310 Hz, $CF_3SO_3^-$), 47.0 (1-[NH(*C*H_3)$_2$]$^+$), 35.9 ([NH_2(*C*H_3)$_2$]$^+$); ν_{max}: 3121, 1595, 1467, 1261, 1243, 1223, 1155, 1030, 883, 838, 765, 743, 693, 637, 574, 550, 516, 503 cm^{-1}; *HRMS*: Found 216.1017, $C_{13}H_{14}NO_2$ requires 216.1019. Crystals for X-ray crystallography grown from acetonitrile had composition of **21.23**.Me_2NH_2.(triflate)$_2$.

N,N-Diisopropyl-1-dimethylammonio-naphthalene-8-carboxamide triflate, 6-H$^+$ $CF_3SO_3^-$

A solution of N,N-diisopropylamide (100 mg, 0.34 mmol) in dry ether (4 mL) at 0 °C under nitrogen was treated with triflic acid (54 mg, 0.36 mmol) in dry ether (2 mL) and stirred for 30 min. A white precipitate of **6-H**$^+$.triflate (86 mg, 57 %) was filtered off and washed with dry ether, m.p.: 141–142 °C dec.; δ_H (400 MHz, $CDCl_3$): 12.88 (1H, br, N-*H*), 8.31 (1H, d, J = 7.8 Hz, Ar-H_1), 8.14 (1H, dd, J = 7.6, 2.1 Hz, Ar-H_1), 8.08 (1H, d, J = 7.8 Hz, Ar-H_1), 7.75 (1H, t, J = 8.0 Hz, Ar-H_1), 7.63–7.68 (2H, m, Ar-H_2), 3.83 (1H, hep, J = 6.4 Hz, C*H*Me_2), 3.75 (1H, hep, J = 6.6 Hz, C*H*Me_2), 3.49 (3H, s, NCH_3), 3.36 (3H, s, NCH_3), 1.67 (3H, d, J = 6.9 Hz, CH_3) 1.57 (3H, d, J = 6.9 Hz, CH_3) 1.34 (3H, d, J = 6.4 Hz, CH_3) 1.08 (3H, d, J = 6.4 Hz, CH_3); δ_C (100.5 MHz, $CDCl_3$): 175.1 (*C*=O), 138.0, 135.9, 133.6, 132.8, 129.5, 127.9, 127.2, 125.8, 122.8, 121.7 (Ar-C_{10}), 120.9 (q, J = 320 Hz, CF_3SO_3), 53.6 (*C*HMe_2), 48.4 (N-*C*H_3), 48.1 (*C*HMe_2), 45.9 (N-*C*H_3), 21.2, 20.7, 19.7 & 19.5 (4 × CH*C*H_3); ν_{max}: 3070, 3010, 2969, 2293 br, 1574, 1528, 1504, 1471, 1451, 1386, 1377, 1340, 1330, 1269, 1256, 1223, 1148, 1133, 1088, 1028, 995, 839, 814, 778, 756, 741, 669, 648, 635, 606, 572 cm^{-1}; found C: 53.50, H: 5.95, N: 6.15 %; $C_{19}H_{27}N_2O.CF_3SO_3$ requires: C: 53.56, H: 6.07, N: 6.25 %.

X-ray crystallography

X-ray diffraction datasets were measured either on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector using the Crysalis software [28] and an Oxford Cryosystems 700 series Cryostream low temperature system at NTU (**18**, **19**, **4-H**.CF_3SO_3, **23**.CF_3SO_3), or at the UK National Crystallography Centre, Southampton University [29] (**6-H**.CF_3SO_3, **21.23**.Me_2NH_2.(CF_3SO_3)$_2$) on a Rigaku AFC12 diffractometer equipped with enhanced sensitivity (HG) Saturn724+ CCD detector mounted at the window of an FR-E+ *SuperBright* rotating anode generator (Mo Kα, λ = 0.71075 Å) with VHF *Varimax* optics (70 μm focus) using Crystal Clear software [30] for data collection and reduction. Structures were solved and refined using the SHELXS and SHELXL suite of programs [31] using the XSEED interface [32]. Molecular illustrations were made with Mercury [33]. Data is deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC-1429425-1429430.

Crystal data for 18.Cl

$C_{20}H_{18}NO_2.Cl$, $M_r = 339.80$, triclinic, $a = 7.1276(3)$, $b = 11.1537(6)$, $c = 11.5211(7)$ Å, $\alpha = 85.312(4)$, $\beta = 73.217(5)$ $\gamma = 73.199(4)°$, $V = 839.47(8)$ Å^3, $Z = 2$, $P\bar{1}$, $D_c = 1.34$ g/cm^3, $\mu = 0.239$ mm^{-1}, T = 150 K, 3668 unique reflections ($R_{int} = 0.027$), 2934 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.060, R_w (F^2, all data) = 0.115. Crystals grown from acetonitrile. The phenyl ring is disordered and modelled over two sites with a 60:40 ratio. The AFIX 66 constraint was used to maintain sensible geometries of the disordered ring. Additionally SIMU, DELU and RIGU restraints were applied to model displacement parameters appropriately using OLEX2 [34].

Crystal data for 19.Cl

$C_{18}H_{22}NO_2.Cl$, $M_r = 319.81$, triclinic, $a = 7.1396(4)$, $b = 11.3139(7)$, $c = 11.7908(7)$ Å, $\alpha = 69.269(5)$, $\beta = 75.628(5)$, $\gamma = 74.139(5)°$, $V = 844.61(9)$ Å^3, $Z = 2$, $P\bar{1}$, $D_c = 1.26$ g/cm^3, $\mu = 0.233$ mm^{-1}, T = 150 K, 3846 unique reflections ($R_{int} = 0.029$), 3170 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.051, R_w (F^2, all data) = 0.107. Crystals grown from acetonitrile.

Crystal data for 4-H.triflate

$C_{14}H_{16}NO_2.CF_3SO_3$, $M_r = 379.35$, orthorhombic, $a = 8.3891(2)$, $b = 15.4896(4)$, $c = 25.0493(7)$ Å, $V = 3255.00(15)$ Å^3, $Z = 8$, *Pbca*, $D_c = 1.55$ g/cm^3, $\mu = 0.258$ mm^{-1}, T = 150 K, 3845 unique reflections ($R_{int} = 0.047$), 2989 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.066, R_w (F^2, all data) = 0.136. Crystals grown from methanol.

Crystal data for 6-H.triflate

$C_{19}H_{27}N_2O.CF_3SO_3$, $M_r = 448.49$, monoclinic, $a = 8.5317(4)$, $b = 13.6323(5)$, $c = 18.9860(13)$ Å, $\beta = 97.220(7)°$, $V = 2190.7(2)$ Å^3, $Z = 4$, $P2_1/c$, $D_c = 1.36$ g/cm^3, $\mu = 0.20$ mm^{-1}, T = 100 K, 4980 unique reflections ($R_{int} = 0.059$), 4325 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.041, R_w (F^2, all data) = 0.110. Crystals grown from acetonitrile.

Crystal data for 21.23.Me_2NH_2.(triflate)$_2$

$(C_{13}H_{12}NO_2).(C_{13}H_{13}NO_2^+).C_2H_7N^+.2CF_3SO_3^-$, $M_r = 1550.445$, monoclinic, $a = 14.3429(5)$, $b = 16.4234(5)$, $c = 15.6915(11)$ Å, $\beta = 112.505(8)°$, $V = 3414.8(3)$ Å^3, $Z = 4$, $P2_1/c$, $D_c = 1.51$ g/cm^3, $\mu = 0.25$ mm^{-1}, T = 100 K, 7816 unique reflections ($R_{int} = 0.054$), 5424 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.048, R_w (F^2, all data) = 0.109. Crystals grown from acetonitrile. The positions of the two unique carboxyl H atoms which are both disordered (50:50) across inversion centres were refined with a SHELXL DFIX restraint of O–H 0.85(1) Å and with an isotropic displacement parameter related to the equivalent isotropic displacement parameter of the attached oxygen atom (x 1.5) in each case.

Crystal data for 23.triflate

$C_{13}H_{13}NO_2.CF_3SO_3$, $M_r = 365.32$, triclinic, $a = 7.6263(4)$, $b = 10.0520(6)$, $c = 10.7161(6)$ Å, $\alpha = 105.593(5)$, $\beta = 101.665(4)$, $\gamma = 98.036(4)°$, $V = 758.32(8)$ Å^3, $Z = 2$, $P\bar{1}$, $D_c = 1.60$ g/cm^3, $\mu = 0.27$ mm^{-1}, T = 110 K, 3069 unique reflections (R_{int}=0.018), 2705 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.036, R_w (F^2, all data) = 0.083. Crystals grown from chloroform.

Acknowledgments: We thank the EPSRC for funding the UK National Crystallography Service and the EPSRC Mass Spectrometry Service for data. We acknowledge the use of the EPSRC funded National Chemical Database Service hosted by the Royal Society of Chemistry [35]. We thank Nottingham Trent University for support including diffraction facilities, and the Erasmus program for supporting AW.

References

[1] W. B. Schweizer, G. Procter, M. Kaftory, J. D. Dunitz. *Helv. Chim. Acta* **61**, 2783 (1978).
[2] J. D. Wallis, R. J. C. Easton, J. D. Dunitz. *Helv. Chim. Acta* **76**, 1411 (1993).
[3] P. C. Bell, W. Skranc, X. Formosa, J. O'Leary, J. D. Wallis. *J. Chem. Soc. Perkin Trans.* **2**, 878 (2002).
[4] D. Pla, O. Sadek, S. Cadet, B. Mestre-Voegtle, E. Gras. *Dalton Trans*., **44**, 18340 (2015).
[5] G. P. Scheimenz. *Z. Naturfor.* **61b**, 535 (2006).
[6] S. D. H. Schumann, M. Hummert, K. C. H. Lange, S. Schutte, B.C. Wassermann, K. Kohler, J. Eichhorn. *Z. Anorg. Allg. Chem.* **630**, 1196 (2004).
[7] P. C. Bell, J. O'Leary, J. D. Wallis, W. B. Schweizer. *J. Chem. Soc. Perkin Trans.* **2**, 13 (2001).
[8] D. R. W. Hodgson, A. J. Kirby, N. Feeder. *J. Chem. Soc.*, *Perkin Trans.* **1** 949 (1999).
[9] N. Mercadal, S. P. Day, A. Jarmyn, M. B. Pitak, S. J. Coles, C. Wilson, G. J. Rees, J. V. Hanna J. D. Wallis. *CrystEngComm* **16**, 8363 (2014).
[10] J. Clayden, C. McCarthy, M. Helliwell. *Chem. Commun*. 2059 (1999).
[11] P. C. Bell, J. D. Wallis. *J. Chem. Soc. Chem. Commun*. 257 (1999).
[12] J. O'Leary, W. Skranc, X. Formosa, J. D. Wallis. *J. Org. Biomol. Chem*. **3**, 3273 (2005).
[13] A. Lari, M. B. Pitak, S. J. Coles, G. J. Rees, S. P. Day, M. E. Smith, J. V. Hanna, J. D. Wallis. *Org. Biomolec. Chem*. **10**, 7763 (2012).
[14] K. B. Birnbaum. *Acta Crystallogr. Sect. B* **28**, 2825 (1972).
[15] G. I. Birnbaum. *J. Am. Chem. Soc.* **96**, 6165 (1974).
[16] W. B. Schweizer, J. D. Dunitz. *Helv. Chim. Acta* **65**, 1547 (1982).
[17] A. Choudhary, K. J. Kamer, R. T. Raines. *J. Org. Chem*. **76**, 7933 (2011).
[18] A. Choudhary, D. Gandla, G.R. Krow, R. T. Raines. *J. Am. Chem. Soc*. **131**, 7244 (2009).
[19] R. W. Newberry, G. J. Bartlett, B. VanVeller, D. N. Woolfson, R. T. Raines. *Protein Science* **23**, 284 (2014).
[20] G. J. Bartlett, R. W. Newberry, B. VanVeller, R. T. Raines, D. N. Woolfson. *J. Am. Chem. Soc*. **135**, 18682 (2013).
[21] A. Choudhary, C. G. Fry, K. J. Kamer, R. T. Raines. *Chem. Commun*. **49**, 8166 (2013).
[22] M. Parvez, I. I. Schuster, *Acta Crystallogr. Sect. C.* **47**, 446 (1991).
[23] I. I. Schuster, A. J. Freyer, A. L. Rheingold. *J. Org. Chem*. **65**, 5752 (2000).
[24] N. Asaad, J. E. Davies, D. R. W. Hodgson, A. J Kirby, L. van Villet, L. Ottavi. *J. Phys. Org. Chem*. **18**, 101 (2005).
[25] R. J. T. Houk, A. Monzingo, E. V. Anslyn. *Acc. Chem. Res*. **41**, 401 (2008).
[26] S. B. Bulgarevich, N. A. Ivanova, D. Y. Movshovich, A. Mannschreck, L. Kiessl, H. Zinner, C. Kiefl. *J. Mol. Struct*. **265**, 417 (1992).
[27] J. Clayden, C. S. Frampton, C. McCarthy, N. Westlund. *Tetrahedron* **55**, 14161 (1999).
[28] CrysAlisPro, Agilent Technologies, Version 1.171.35.15 (release 03-08-2011 CrysAlis 171.NET).
[29] S. J. Coles, P. A. Gale. *Chem. Sci*. **3**, 683 (2012).
[30] Crystal Clear-SM Expert 2.0 r11 (Rigaku, 2011).
[31] G. M. Sheldrick. *Acta Crystallogr. Sect. A* **64**, 112 (2008).
[32] L. J. Barbour. "X-Seed – A software tool for supramolecular crystallography" *J. Supramol. Chem*. **1**, 189 (2001).
[33] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek. *J. Appl. Crystallogr.* **39**, 453 (2006).
[34] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H Puschmann. *J. Appl. Cryst*. **42**, 339 (2009).
[35] F. H. Allen. *Acta Crystallogr. Sect. B* **58**, 380 (2002).