

The shortest C–H···O hydrogen bonds yet determined by single crystal neutron diffraction: a structural study of two phosphonium aryloxides

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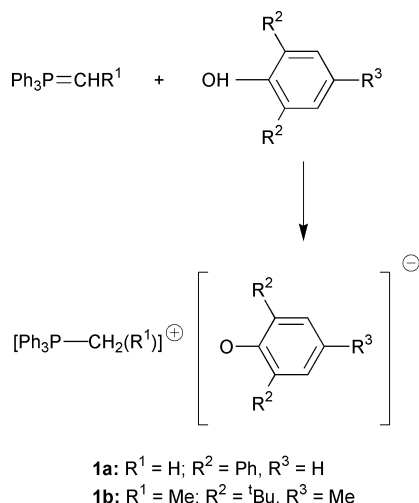
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The structures of two phosphonium aryloxides have been determined by neutron diffraction at 20 K and reveal extensive aggregation in the solid state *via* very short C–H···O and C–H··· π interactions, including the shortest C–H···O distance yet determined by neutron diffraction.

Much interest is focused on the systematic study of solids in which C–H···X hydrogen bonding is present, since such interactions have been shown to be capable of playing a decisive role in the supramolecular structure of solids.¹ Amongst compounds able to form strong C–H···X hydrogen bonds, and those that have been most extensively studied, are X₃CH (where X = Cl, NO₂, *etc.*)² and R–C \equiv C–H.^{1a} However, other systems containing acidic C–H groups have also been shown to participate in structurally important C–H···X interactions.³ One such class of compound, whose study has so far been limited, is Group 15 ‘onium’ cations. We have shown that the protonation of triphenylphosphonium alkylides with OH-, NH- and PH-acidic organic compounds, provides a facile and versatile route to hydrocarbon soluble, crystalline phosphonium aryloxides **1** (Scheme 1), amides and phosphides, respectively.^{4–6} In these salts the combination of many potential C–H donor groups and the availability of electron rich acceptor anions, provides an ideal platform for the study of C–H···X interactions in the absence of stronger, more structurally dominant interactions. In order to fully characterise this type of C–H···O interaction we have now performed



Scheme 1

low-temperature (20 K) neutron diffraction structures of two phosphonium aryloxides, [(Ph₃PMe)⁺(OC₆H₃Ph₂-2,6)[−]]₂ **1a** and [(Ph₃PEt)⁺(OC₆H₂Bu₂-2,6-Me-4)[−]]_∞ **1b**.

Deprotonation of 2,6-diphenylphenol with triphenylphosphonium methyllide in toluene: acetonitrile yielded a crystalline yellow solid[†] which was revealed to be the expected salt **1a** by X-ray crystallography. Of particular note in the X-ray structure were exceptionally short C···O distances which prompted us to perform a low-temperature (20 K) neutron diffraction study[‡] in order to fully characterise the hydrogen bonding. All structural parameters discussed below relate to this latter study. The molecular geometries of both cation and anion are as expected. On the supramolecular level (Fig. 1), **1a** adopts a C–H···O hydrogen bonded dimeric structural motif similar to that previously observed for a phosphonium aryloxide.⁴ Two chemically similar but crystallographically independent centrosymmetric dimers are found in the crystallographic unit cell and only one of these will be discussed further. Within each dimer, the methyl group of each cation interacts with the two anionic oxygen centres of the anions *via* C(alkyl)–H···O hydrogen bonds. This (···H–C–H···) bridge is slightly asymmetric. The four-coordination of each oxygen atom is completed by one C(aryl)–H···O interaction. Of particular interest in **1a** are the short H···O distances clustered around 2 Å (Table 1), which are at the lower limit for previously observed ‘strong’ C–H···O hydrogen bonds.^{1a} The shortest hydrogen bond in **1a**, H212···O21 [1.935(5) Å], is over 5% shorter than any other found for a neutron structure in the CSD⁷ (in the structure of 1-methylthymine,⁸ CSD refcode: METHYM01, shortest C–H···O distance, 2.045 Å). The unusual shortness of the hydrogen bonding in **1a** may be attributed to a number of interrelated factors including: an electrostatic reinforcement of the bonding; an inductive enhancement of acidity of the methyl group due to the presence of a charged heteroatom; and the presence of an extremely basic oxygen centre. The C–H distances of those groups involved in hydrogen bonding do not appear to be significantly elongated. This emphasises the electrostatic nature of the bonding between C–H and O, and argues against a significant contribution to the interaction from covalent three centre–two electron bonding. It is also worthy of note that the neutron data provide no evidence for disorder between C–H···O and O–H···C hydrogen bonding in **1a** in the solid state.

Increasing the steric bulk both of the phosphonium alkyl group and the groups *ortho* to the oxygen atom of the anion reduces the degree of aggregation by the mode described

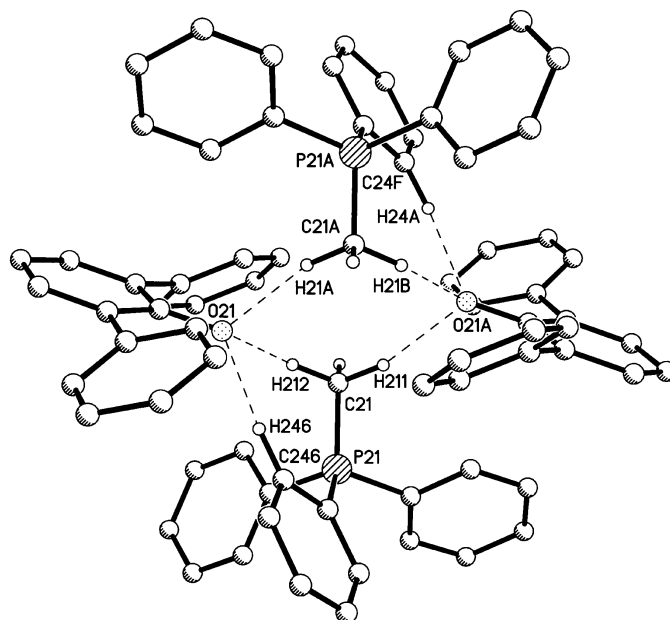


Fig. 1 The structure of **1a** (only one of two geometrically similar dimers shown), H-atoms not involved in H-bonding omitted for clarity (see Table 1 for H-bond parameters).

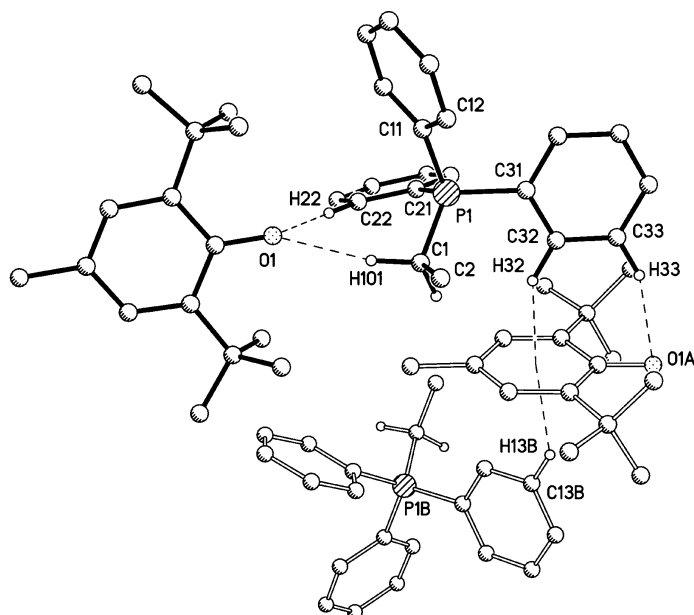


Fig. 2 The structure of **1b**, H-atoms not involved in H-bonding omitted for clarity (see Table 1 for H-bond parameters).

Table 1 Geometric parameters for C–H···O and C–H··· π hydrogen bonds in **1a** and **1b**

Compound	Interaction	C–H distance/ Å	H···X distance/ Å	C–H···X angle/ °
1a	C11–H111···O11C ^a	1.100(5)	1.968(5)	167.7(4)
1a	C11–H112···O11 ^a	1.098(5)	2.034(5)	161.4(4)
1a	C142–H142···O11C ^a	1.090(4)	2.166(4)	168.2(4)
1a	C21–H211···O21A	1.102(4)	2.119(5)	157.8(4)
1a	C21–H212···O21	1.105(5)	1.935(5)	166.9(4)
1a	C246–H246···O21	1.095(5)	2.118(5)	174.0(4)
1b	C1–H101···O1	1.103(3)	2.271(3)	168.3(2)
1b	C22–H22···O1	1.092(3)	1.998(3)	179.3(3)
1b	C13B–H13B··· π	1.089(3)	2.419(3) ^b	145.0(3) ^c
1b	C32–H32··· π	1.088(3)	2.341(3) ^b	144.2(3) ^c
1b	C33–H33··· π	1.088(3)	2.353(3) ^b	160.0(2) ^d

^a Not shown in figure. ^b Perpendicular distance from the H atom to the plane of the ring (C41A–C46A). ^c Angle between the C–H bond and the centroid of C41A to C46A. ^d Angle between the C–H bond and O1A.

above. An X-ray structure and then low-temperature (20 K) neutron diffraction study§ of $[(\text{Ph}_3\text{PEt})^+(\text{OC}_6\text{H}_2\text{Bu}_2-2,6-\text{Me}_4)^-]_\infty$ **1b** (Fig. 2) reveals that, although the mode of cation–anion association resembles that seen in the monomeric sub-units of **1a**, dimerisation of these units does not occur. However, the electronic factors favouring aggregation prevail, and for **1b** an alternative mode of association operates. Longer range, out-of-plane C–H $\cdots\pi$ interactions take place between aryl C–H groups of the cation and the electron-rich π -system of both faces of the anion. Adjacent *ortho*- and *meta*-C–H groups of one phosphonium cation (H32 and H33, Fig. 2) interact with one face of the anion's π -system, including the coplanar p-orbital of O1. The distances involved (Table 1) are at the lower end of the range seen previously for similar interactions.^{1d} Not only the distances but also the orientation of the groups involved suggest an attractive interaction. First, the H33 \cdots O1A bond vector lies along the only open approach to the anionic oxygen atom: all other approaches are blocked by the organic framework of the monomeric unit. Second, the two aryl groups are almost orthogonal to each other [angle between the planes defined by C31–C36 and C41A–C46A = 79.7(1)°]. Third, H32 and H33 are essentially equidistant from the plane defined by the ring C41A–C46A [2.341(3) and 2.353(3) Å for H32 and H33, respectively]. Finally, H32 lies almost directly above the centroid of C41A–C46A.

The other face of the anion is also involved in a C–H $\cdots\pi$ interaction with H13B, a *meta*-C–H group of a symmetry related cation, which completes an unusual, though not unprecedented,^{1d} C–H $\cdots\pi\cdots$ H–C interaction. Again, the relative orientation of the groups involved suggests an attractive interaction. The two aryl groups are orthogonal to each other [angle between the planes defined by C11B–C16B and C41A–C46A = 86.4(1)°], C11B–C16B is also oriented such that only one hydrogen atom (H13B) comes into close contact with C41A–C46A. At this face no additional interaction with oxygen is possible since close approach to O1 is blocked by the cation (specifically by C21–C26).

In summary, the characterisations of **1a** and **1b** by neutron diffraction allow the following conclusions to be drawn: (i) organophosphonium cations are strong and versatile C–H hydrogen bond donors, *via* both alkyl and aryl C–H groups; (ii) chelation of the anionic oxygen centre by alkyl and *ortho*-phenyl C–H groups of the cation is a structural motif common to 'monomeric' units of **1a** and **1b**; (iii) steric inhibition of this mode of aggregation results in the observation of other, less conventional, secondary interactions; (iv) precise location of the hydrogen atoms in these salts suggests that the C–H \cdots O hydrogen bonds are predominantly electrostatic in nature and also rules out the possibility of disorder of the H atom in these very short interactions.

Acknowledgements

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Notes and references

† *Synthesis of phosphonium salts 1a*: Dry toluene (10 mL) was added under nitrogen to Ph_3PCH_2 (0.69 g, 2.5 mmol) and 2,6-diphenylphenol (0.62 g, 2.5 mmol). On stirring a pale yellow precipitate in a yellow solution was obtained. Addition of more toluene (10 mL) and heating afforded no change. On addition of acetonitrile (5 mL) the precipitate dissolved to give a clear orange solution. Standing at room temperature overnight yielded a crop of yellow blocks (0.9 g, 70%). Mp 205–207 °C. Anal. calc. % (found %) $\text{C}_{37}\text{H}_{31}\text{OP}$: C, 85.1 (84.1); H, 5.9 (5.6); P, 5.9 (6.0). ^1H NMR (250 MHz, 25 °C, C_6D_6): δ 3.0 (3H, d, CH_3), 6.7–8.2 (36H, m, ArH). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.2 MHz, 25 °C, C_6D_6): δ 25.7 (s). **1b**: Dry thf (12 mL) was added under nitrogen to $\text{Ph}_3\text{PC}(\text{Me})\text{H}$ (0.73 g, 2.5 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (0.55 g, 2.5 mmol). Stirring at room temperature resulted in the formation of an orange precipitate which, on warming, dissolved to give a clear, deep red solution. Standing at room temperature overnight yielded a crop of orange blocks (0.4 g 32%). Mp 189–191 °C. Anal. calc. (found) $\text{C}_{35}\text{H}_{43}\text{OP}$: C, 82.4 (81.3); H, 8.4; P, 6.1 (6.0) %. ^1H NMR (200 MHz, 25 °C, C_6D_6): δ 1.1 (3H, d, PCH_2CH_3), 1.8, (18H, s, ArC_4H_9), 2.6 (3H, s, ArCH_3), 4.5 (2H, dr s, PCH_2CH_3), 7.0–7.5 (11H, m, ArH), 7.6 (6H, m, *ortho* ArH of $\text{Ph}_3\text{PCH}_2\text{Me}^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.2 MHz, 25 °C, C_6D_6): δ 26.3 (s).

‡ Crystal data for **1a**: crystal dimensions 4.9 × 3.9 × 1.1 mm, $\text{C}_{37}\text{H}_{31}\text{OP}$, $M = 522$, triclinic, $P\bar{1}$, $a = 13.430(1)$, $b = 13.748(1)$, $c = 18.444(1)$ Å, $\alpha = 88.310(3)$, $\beta = 70.157(3)$, $\gamma = 62.542(3)^\circ$, $U = 2809.2(1)$ Å³, $Z = 4$, $D_c = 1.234$ g cm^{−3}, $\lambda = 1.3137$ Å (Ge 115 monochromatic thermal neutrons), $T = 20$ K (Displex cryorefrigerator), $\mu = 2.13$ cm^{−1}. 12 265 reflections ($-14 > h > 15$, $-15 > k > 16$, $-21 > l > 21$, $2\theta_{\text{max}} = 100.6^\circ$) were collected on the D19 diffractometer at ILL. 8567 unique reflections, corrected for absorption by Gaussian integration using the D19ABS program⁹ ($R_{\text{int}} = 0.0328$) were used to refine the starting model (1262 parameters) obtained from X-ray diffraction data. All atoms were given anisotropic displacement parameters and refinement on F^2 converged to $R_1 = 0.0440$, $wR_2 = 0.1319$ and $S = 1.13$.

§ Crystal data for **1b**: crystal dimensions 3.5 × 3.5 × 2.4 mm, $\text{C}_{35}\text{H}_{43}\text{OP}$, $M = 510$, orthorhombic, $Pbca$, $a = 18.570(1)$, $b = 17.220(1)$, $c = 19.030(1)$ Å, $U = 6085.3(6)$ Å³, $Z = 8$, $D_c = 1.113$ g cm^{−3}, $\lambda = 1.3137$ Å (Ge 115 monochromatic thermal neutrons), $T = 20$ K (Displex cryorefrigerator), $\mu = 2.73$ cm^{−1}. 11 054 reflections ($-10 < h < 21$, $-6 > k > 20$, $-21 > l > 22$, $2\theta_{\text{max}} = 101.3^\circ$) were collected on the D19 diffractometer at ILL. 4995 unique reflections, corrected for absorption by Gaussian integration using the D19ABS program⁹ ($R_{\text{int}} = 0.0378$) were used to refine the starting model (722 parameters) obtained from X-ray diffraction data. All atoms were given anisotropic displacement parameters and refinement on F^2 converged to $R_1 = 0.0357$, $wR_2 = 0.0738$ and $S = 1.17$. CCDC reference number 440/187. See <http://www.rsc.org/suppdata/nj/b0/b001433h/> for crystallographic files in .cif format.

- (a) T. Steiner, *Chem. Commun.*, 1997, 727; (b) F. H. Allen, J. A. K. Howard, V. J. Hoy, G. R. Desiraju, D. S. Reedy and C. C. Wilson, *J. Am. Chem. Soc.*, 1996, **118**, 4081; (c) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2328; (d) R. Hunter, R. H. Hauelsen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566; (e) C. A. Hunter, *Chem. Soc. Rev.*, 1994, 101; (f) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397; (g) G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
- V. R. Pedireddi, G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 988; G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1990, 454; G. R. Desiraju, 1989, 179.
- M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.*, 1996, 2285.
- M. G. Davidson, *J. Chem. Soc., Chem. Commun.*, 1995, 919.
- M. G. Davidson and S. Lamb, *Polyhedron*, 1997, **16**, 4393.
- M. G. Davidson, K. B. Dillon, J. A. K. Howard, S. Lamb and M. D. Roden, *J. Organomet. Chem.*, 1998, **550**, 481.
- F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1.
- A. Kvik, T. F. Koetzle and R. Thomas, *J. Chem. Phys.*, 1974, **61**, 2711.
- D19ABS, J. C. Matthewman, P. Thompson and P. J. Brown, *J. Appl. Crystallogr.*, 1982, **15**, 167.