Phosphonium ylides as hydrogen bond acceptors: intermolecular C–H···C interactions in the crystal structure of triphenylphosphonium benzylide

Andrei S. Batsanov, Matthew G. Davidson,* Judith A. K. Howard, Sarah Lamb and Christian Lustig

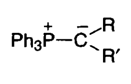
Department of Chemistry, Science Laboratories, Durham, UK DH1 3LE

A pairwise alignment of molecules in the crystal structure of the title ylide suggests the existence of mutual C–H···C interactions between acidic *o*-Ph groups of one molecule and the basic carbanionoid centre of the other, an interpretation which is supported by examination of previously reported X-ray data.

The influence of 'strong' X–H···Y hydrogen bonds (*e.g.*, where X and Y = N or O) over the structure, physical properties and reactivity of organic compounds is well established[1] and it is increasingly evident that weaker C–H···X interactions can also play a decisive role in the structure of solids.[2] Consequently, considerable interest is now focused on the study of such interactions. C–H···X interactions, where X = O or N, are the most commonplace, though it has also been shown that carbon-based π-bonded systems such as alkynes[2b,3] and arenes[4] can also function as acceptors to acidic C–H groups. Reports of other C–H···C interactions are rare and they have only recently been characterised definitely in the crystal structures of two closely related bis(carbene)–proton complexes.[5] Here we report the crystal structure of triphenylphosphonium benzylide **1a** in which a pairwise alignment of molecules suggests the possibility of intermolecular C–H···C interactions between acidic phenyl C–H groups and the basic carbanionoid centre of the ylide. To our knowledge, this is the first report of a phosphonium ylide functioning as a hydrogen bond acceptor in the solid state.

While the electronic structure of ylides remains a matter of some debate, theoretical, structural and experimental evidence all concur[6] that a high degree of negative charge resides on the ylidic carbon of phosphonium ylides **1**. This property renders ylides highly basic and suggests their potential as hydrogen bond acceptors. This has already been recognised: Schmidbaur *et al.* considered C–H···C hydrogen bonding as an explanation for the rapid 'proton scrambling' observed in trialkylphosphonium alkylides though a crystal structure of $Pr^i_3P{=}CMe_2$ provided no supporting evidence;[7] and hypothetical, isoelectronic nitrogen ylides have recently been calculated (*ab initio*) to form remarkably stable 1 : 1 adducts with acetylene and even methane *via* C–H···C (ylide) interactions.[8]

In order to further examine this aspect of ylide chemistry, and as part of our wider interest in both ylides[9] and hydrogen bonding,[10] we carried out a single crystal X-ray study of **1a**. A small crop of X-ray quality crystals was obtained by refrigeration of a dilute THF–hexane solution of **1a** prepared according to established procedures.[11] On the molecular level, the X-ray structure† is unexceptional. The P(1)–C(7) bond length [1.696(3) Å] is expected for a non- or semi-stabilised ylide[6] and the substituents R and R′ (H and Ph) are coplanar with the ylidic P(1)–C(7) bond [sum of angles around C(7), 360.0°]. This is expected for a semi-stabilised ylide but contrasts with the pyramidalisation usually found in non-stabilised ylides.[6] Most striking in the structure of **1a**, however, is the pairwise alignment of molecules resulting in an acidic *o*-PhH donor atom of one molecule apparently interacting with the carbanionoid carbon acceptor atom of another‡ [C(36)–H(36)···C(7a), D = 3.832(5), d = 2.80 Å, θ = 159°]. This mutual interaction results in the dimeric aggregation shown in Fig. 1, a common structural motif in hydrogen bonding. Though distance alone is not a wholly satisfactory criterion by which to judge the validity of weak hydrogen bonds, this interaction falls within the accepted geometry of C–H···X interactions. For example: in evaluating the significance of C–H···X distances (X = N, O, or the mid point of C≡C) in crystals, Steiner recently concluded that 'a cut off value of H···X as long as 2.8 Å or even longer is therefore justified and necessary';[12] d in **1a** is approximately 0.2 Å shorter than the H···C interactions held to be responsible for the herringbone packing of benzene;[13] and θ in **1a** is consistent with the observation that for C–H···X hydrogen bonds this angle tends to cluster in the range 150–160°.[2a] Also in this context, and since the distance of a C–H···X interaction has been shown to be more dependent on the C–H acidity than on the X basicity,[14] it is perhaps significant that d in a C–H···π interaction involving a similar donor to **1a** (*o*-PhH of a $Ph_3PCH_3^+$ cation) and the π-system of a furan ring was reported recently to be 2.79 Å.[4a] Another attribute characteristic of C–H···X interactions is their electrostatic directionality. That is, the H atoms tend to point towards the lone pairs of the acceptor atom.[2a] In **1a** this is the case, though the H···C bond vector is not quite perpendicular to the plane defined by P(1), C(7) and H(7), but is slightly



$$Ph_3\overset{+}{P}-\overset{-}{C}\begin{smallmatrix}R\\R'\end{smallmatrix}$$

1a R = H, R′ = Ph
b[16] CRR′ = $\lhd$
c[19] R = R′ = H

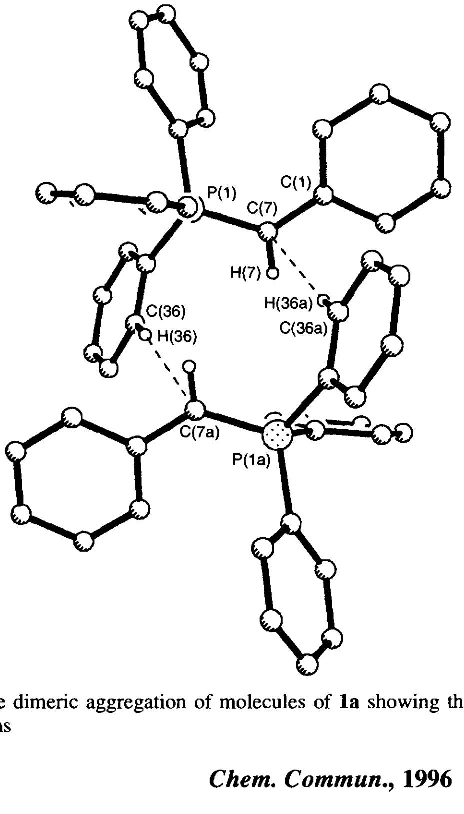


Fig. 1 The dimeric aggregation of molecules of **1a** showing the C–H···C interactions

inclined away from the Ph_3P moiety [P(1)–C(7)–H(36a), 118.5°; C(1)–C(7)–H(36a), 75.1°; H(7)–C(7)–H(36a), 74.2°). Whether this is an accurate reflection of the electronic environment around C(7) or simply a sterically induced deformation caused by the Ph_3P groups is unclear.

In a search for other similar interactions, we have examined previously reported crystal structures of phosphonium ylides. A search of the Cambridge Structural Database (October 1995 release)[15] for ylides containing at least one phosphorus-bound Ph and (other than the phosphonium centre) containing only C and H atoms, resulted in five hits which were all retrieved and examined manually. Of these five ylides, triphenylphosphonium cyclopropylide, **1b**,[16] contains features of particular note in the present context.§ In the structure of **1b** there are two short intermolecular C–H···C contacts between *o*-PhH atoms of one molecule and the carbanionoid C atom of another. One is of a similar length to that found in **1a** but the other appreciably shorter [C(15b)–H(15b)···C(4a), D = 3.833, d = 2.81 Å, θ = 159° and C(21b)–H(21b)···C(4a), D = 3.620, d = 2.58 Å, θ = 161°]. As with **1a**, the geometries are consistent with those found previously for C–H···X hydrogen bonds and each ylide acts as both a donor and an acceptor. Here though polymeric helical chains of molecules result (Fig. 2)—again a rational topology for hydrogen bonding. It is noteworthy that **1b** is exceptional among structures of phosphonium ylides in the degree of deviation (58°) of the substituents bound to C(4) (in this case the two CH_2 groups of a cyclopropyl ring) from the PCRR′ plane. It is an open question as to whether the C–H···C interactions found in **1b** are partially responsible for this extreme pyramidalization or whether it is a manifestation of some other effect which is then simply exploited by the acidic H atoms. As with **1a**, the electrostatic directionality of the interactions is clear: the 'lone pair' on carbon can be imagined to bisect the two H···C bond vectors [most apparent for C(4b), Fig. 2].

The range at which the interactions found in **1a** and **1b** operate suggests a similar strength to C–H···π interactions. This is supported by the structure of **1c** which *preferentially* aggregates *via* C–H···π interactions, and contrasts with the strength estimated by theoretical calculations.[8]

A comparison of the molecular geometries of **1a** and **1b** lends further credence to the validity of the proposed interactions. For **1a**, where only one Ph group is involved as a donor, there is approximately threefold rotational symmetry around an axis defined by the ylidic bond [C(7)–P(1)] resulting in the expected propeller-like arrangement of Ph groups around P(1). For **1b**, however, where two Ph groups chelate a neighbouring carbon acceptor [C(4)], the molecules are locked in an unusual conformation containing a (non crystallographic) mirror plane through C(33), C(3), P(1) and C(4) [most apparent for molecule (a), Fig. 2].

We are currently further investigating the nature of such interactions, both experimentally and theoretically.

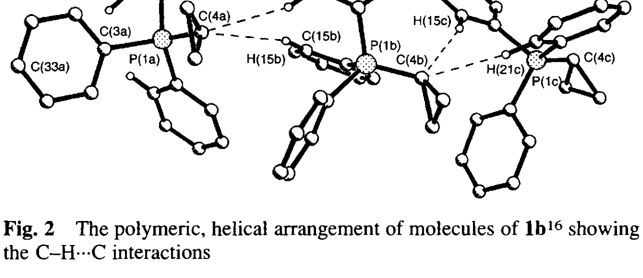


Fig. 2 The polymeric, helical arrangement of molecules of **1b**[16] showing the C–H···C interactions

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Footnotes

† *Crystal data* for **1a**: $C_{25}H_{21}P$, M = 352.39, orange plate-like crystal of 0.3 × 0.2 × 0.08 mm, T = 150(2) K, monoclinic, a = 9.447(1), b = 11.005(1), c = 18.516(1) Å, β = 91.39(1)°, U = 1924.4(3) Å^3 (from 290 reflections 12 < θ < 23°), space group $P2_1/c$, Z = 4, D_c = 1.22 g cm^{-3}, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 1.5 cm^{-1}; data collection on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode, $2\theta \leqslant 48°$, 10 064 total, 3023 unique, 2161 observed [$I > 2\sigma(I)$] data, R_{int} = 0.069. The structure was solved[17] by direct methods and refined[17] by full-matrix least-squares against F^2 (non-H atoms anisotropic, all H isotropic, 320 variables/2908 data) to wR (F^2, all data) = 0.121, goodness-of-fit 1.13, R(F, obs. data) = 0.051; $\Delta\rho_{max}$ = 0.23 eÅ^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/148.

‡ In all subsequent description of C–H···X hydrogen bonds, D is defined as the C···X distance, d as the H···X distance and θ as the C–H···X angle. All parameters are based on the normalised C–H bond lengths of 1.08 Å.

§ The structure of **1c**,[18] is also of interest: rather than C–H···C (ylide) interactions, the two independent molecules of the crystallographic asymmetric unit aggregate *via* mutual C–H···π interactions involving a *m*-PhH atom of one and the phenyl π-system of the other [average of two C–H···(ring centroid) distances (Å) and angles (°): D = 3.580, d = 2.55, θ = 159].

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