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Piperonylic anhydride: Isolation and conformational analysis by X-ray crystallography and density functional theory calculations

Maja W. Chojnacka^a, Alan J. Lough^{b,1}, R. Stephen Wylie^a, Robert A. Gossage^{a,*}

^a Department of Chemistry & Biology, Ryerson University, 350 Victoria Street, Toronto, ON, Canada M5K 2B3
^b Department of Chemistry, University of Toronto, Toronto, ON, Canada M5S 3H6

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ABSTRACT

The title compound (1), a symmetrically substituted acyclic anhydride, is shown to crystallise in the monoclinic space group $P2_1/n$ with a = 4.7032(1) Å, b = 17.8748(6) Å, c = 15.6869(5) Å, $\beta = 98.3980(17)^{\circ}$ and V = 1304.64(7) Å³. There are four molecules in the unit cell. Bond lengths and angles of 1 are comparable to the limited number of benzoic anhydride crystal structures that have been previously disclosed. Compound 1 adapts a *syn*-conformation in the solid-state with a pseudo-torsion angle for the O=C···C=O groupings of approximately 25.1°. This structure is compared to other benzoic anhydride (BA) materials that have been structurally elucidated either via single crystal X-ray diffraction methods and/or examined from a theoretical perspective. Calculations at the DFT level (B3LYP 6-311G^{**}) for a theoretical gas phase molecule of 1 reveals a similar overall global structure to that observed in the solid-state; these results suggest that crystal packing effects are negligible with respect to the observed ground state *syn*-conformation in the solid phase. Compound 1 also represents the first structurally characterised di-substituted benzoic anhydride.

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1. Introduction

Anhydrides represent an important class of organic compounds which have found widespread use as synthetic intermediates, in polymer chemistry [1–13] and as precursor molecules for applications in materials science [14]. The OC—O—CO fragment can engender a large dipole moment to the anhydride and this aspect has been exploited in, for example, the design of novel liquid crystals [15]. Despite the widespread use of anhydrides, very few diaryl anhydrides, *i.e.*, derivatives of the parent compound benzoic anhydride (BA: Fig. 1) [16], have been crystallographically characterised [17–25].

During a series of reactions involving the acylation of heterocyclic bases involving various benzoyl chlorides (Fig. 2: [26]), we noted the formation of a minor by-product upon the specific application of piperonyloyl chloride (*i.e.*, 3,4-(CH₂O₂)C₆H₃COCl). This product readily crystallised and displayed a high degree of symmetry *via* NMR analysis. Furthermore, the compound was devoid of any molecular fragments of the organic base. Herein, we detail the solid-state structure of this material which has been identified as piperonylic anhydride (**1**). Compound **1** represents the first such

* Corresponding author.

di-substituted symmetric benzoic anhydride to be characterised by single crystal X-ray diffraction methods. The structure of **1** is compared and contrasted to the relatively few benzoic anhydrides that have been examined in the solid-state (*i.e.*, X-ray) and its gas phase structure is likewise examined by density functional theory (DFT) at the B3LYP 6-311G^{**} level and these data are then compared to that calculated for BA itself.

2. Results and discussion

2.1. Synthesis and characterisation

A facile method for the production of acyl enamines (Eq. (1): Fig. 2) involves the acylation of weakly basic azoles such as benzoxazoles, benzothiazoles [26a] or oxazolines [26b] using, for example, benzoyl chlorides. The products of this coupling are useful intermediates for applications in heterocyclic syntheses [26–28].

Using the standard reaction protocols [26b] but employing 2,4,4-trimethyl-2-oxazoline as the azole and piperonyloyl chloride (Fig. 1: $R = C_6H_3(O_2CH_2)$ -3,4), the resulting crude product mixture contained not only the expected acyl enamine [28] but a second minor product (isolated yield: 10%). This latter material displayed a high retention factor (R_f) as shown by TLC analysis (see Section 4). Isolation of this rapidly mobile material presented a light yellow solid (1) displaying an IR spectrum with absorbances characteristic [16] of an anhydride (KBr; cm⁻¹: 1768 m, 1707 m). Benzoic anhy-



E-mail addresses: alough@chem.utoronto.ca (A.J. Lough), gossage@ryerson.ca (R.A. Gossage).

¹ Corresponding author concerning the crystallographic work.

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Fig. 1. The syn- and anti-isomers of benzoic anhydride.



Fig. 2. The general reaction scheme leading to the formation of by-product 1.



Fig. 3. Schematic representations of the various hypothetical structural forms 1.

drides can be produced in a number of ways [1,2] but are typically formed by the stoichiometric treatment of benzoyl chlorides and the corresponding acid in the presence of base [2] or *via* benzoic acid reactions with acetic anhydride [15]. However, such compounds can also be formed by the reaction of benzoyl chlorides and amine bases in "wet" solvents. This latter scenario appears to be the case here as we did not pre-dry the reaction solvent (MeCN) nor the NEt₃ used in the reaction mixture. Such protocols are typically unnecessary to facilitate high yields of the desired acyl enamines [26–28]. To unequivocally characterise the nature of 1, we carried out a single crystal X-ray diffraction study of a sample of the said re-crystallised material.

2.2. Structural considerations

Compound **1**, piperonyl anhydride (Fig. 4), forms monoclinic crystals from $CHCl_3$ /hexanes mixtures. These crystals are of space group $P2_1/n$ with four molecules of **1** in the unit cell. Table 1 contains the general crystal parameters for **1** and Table 2 contains a list of bond lengths and angles for a unit cell molecule of **1**.

Table 1

General crystal parameters for compound 1.

Empirical formula	C ₁₆ H ₁₀ O ₇
Formula weight	314.24
Crystal system	Monoclinic
Crystal colour	Pale yellow
Crystal size (mm ³)	$0.20\times0.12\times0.06$
Space group	$P 2_1/n$
a (Å)	4.7032(1)
b (Å)	17.8748(6)
<i>c</i> (Å)	15.6869(5)
α (°)	90.00
β (°)	98.3980(17)
γ (°)	90.00
V (Å ³)	1304.64(7)
Ζ	4
Density (calc.: g/cm ³)	1.600
Abs. coeff. (mm^{-1})	0.128
F(000)	648
Temperature (K)	150(1)
Θ (minmax.)	2.62–27.49°
Dataset [h, k, l]	-6/6, -23/23, -20/20
Total data, unique data, <i>R</i> (int)	11,337, 2967, 0.0465
Observed data (> $2\sigma(I)$)	2967
Completeness to theta = 27.49°	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.002 and 0.904
Refinement method	Full-matrix least-squares on F ²
N _{Data} , N _{Restraints} , N _{Parameters}	2967, 0, 208
GoF (F^2)	1.035
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0505, wR2 = 0.1209
R indices (all data)	<i>R</i> 1 = 0.0921, <i>wR</i> 2 = 0.1480
Largest diff.: peak, hole (e. Å ³)	0.247, -0.250



Fig. 4. ORTEP representation of a molecule of 1 found in the unit cell showing the atomic numbering scheme.

Table 2

Selected bond lengths (Å) and angles (°) for **1** as measured (X-ray) and calculated (DFT: *syn*-[1,2] form). Estimated standard deviations are shown in parentheses.

	X-ray	DFT (B3LYP 6-311G**)
O(3)-C(8)	1.201(2)	1.197
O(4)—C(9)	1.390(2)	1.396
O(4)-C(8)	1.395(2)	1.395
O(5)—C(9)	1.200(2)	1.197
C(5)-C(8)	1.473(3)	1.479
C(9)-C(10)	1.476(3)	1.480
C(9)-O(4)-C(8)	122.90(16)	120.09
O(2) - C(1) - O(1)	107.05(16)	107.57
O(3) - C(8) - O(4)	122.88(18)	122.26
O(3)-C(8)-C(5)	126.28(17)	125.72
O(4)-C(8)-C(5)	110.79(17)	111.95
O(5)-C(9)-O(4)	123.85(17)	122.27
O(5)-C(9)-C(10)	125.07(18)	126.01
O(4)-C(9)-C(10)	111.02(17)	111.66
O(6)-C(13)-O(7)	107.74(15)	107.55

An ORTEP [29] diagram is presented in Fig. 4 which shows the atomic numbering scheme. Although it is known that acyclic anhydrides can crystallise with almost unrestricted conformations (Fig. 3) [19,22], compound **1** is shown to adopt a *syn*-configuration in relation to the orientation of the two C=O groupings attached to the central anhydride oxygen atom (i.e., O4). The syn-conformational isomer is also displayed in the solid-state for several other related anhydrides such as 5,5'-Di(anthracenecarboxylic) anhydride [23], aspirin anhydride [20], and the m-NO₂ [21], o-NO₂ [19], p-Br [14,17] and p-Cl [18] derivatives of benzoic anhydride (BA) itself.² Previously reported molecular calculations [15], at both the MM2 and AM1 levels of theory, have predicted a higher (gas phase) stability for the syn-form of BA. Calculations at a higher level of theory herein (DFT: B3LYP 6-311G**) of both BA and 1 confirm a similar global structure to that suggested earlier [15] for BA and the syn-form observed in the solid-state (see Supplementary material) for **1**. Unlike the situation with BA, the *syn*-conformation of **1** can be further differentiated by the orientation of the two, essentially co-planar, aromatic rings; these rotational isomers are depicted and denoted in Fig. 3 as the syn-[1,2], syn-[1,1] and syn-[2,2] forms. Crystallographically characterised **1** takes the *syn*-[1,2] form (Fig. 4) with independent and mutually rotated aromatic rings. The pseudo-torsion angle is 03=C8...C9=05 in solid 1 is 25.1° which can be compared to that of, for example, 27.7° found in onitrobenzoic anhydride [19]. As mentioned earlier, the two aromatic rings of **1** are not truly co-planar; a torsion angle of 17.2° is noted as measured along the O3-C8-O4-C9 vector. The bond lengths and angles of **1** (Table 2) are typical in relation to those examples mentioned above [15,18-25] and are otherwise unsurprising. Specifically, the C=O and C-O bonds lengths are well within the expected ranges [30] for an anhydride. Predictably, the gas phase calculations of 1 suggests that all three syn-structural forms are very close in energy (relative energies: [1,1] = 0.00 kcal/mol; [1,2] = +0.25 kcal/mol and [2,2] = +0.33 kcal/mol) but obviously imply that in the gas phase the *syn*-[1,1] isomer would be preferred. In solution (room temperature: CDCl₃), only one aromatic group is noted and hence rapid rotation and/or local symmetry higher than that of point group C_1 (*i.e.*, syn-[1,2]) is present (see Section 4). Of further interest are the calculated parameters of the syn-[1,1] isomer which leads to a situation that is characterised (Supplementary material) as having with the smallest O3–C8–O4–C9 torsion angle, most constrained O3=C8...C9=O5 pseudo-torsion angle and resulting lowest calculated dipole moment (4.32 Debye) of the three synforms. When compared to the observed solid-state data, DFT (of the *syn*-[1,2] form) does a reasonable job at estimating the observed solid-state bond lengths and angles (Table 2) of **1**.

The estimated dipole moment (DFT: B3LYP 6-311G^{**}) for **1** is calculated as 5.20 Debye (*syn*-[1,2] form); a larger value than that calculated for BA (4.27 Debye) itself.³ This difference is no doubt a reflexion of the presence of the electron withdrawing O_2CH_2 groups bridging both of the *meta*- and *para*-aromatic positions of **1**. Net atomic charges (Mulliken: *syn*-[1,2] form) calculated at oxygen atoms O3 (-0.292) and O5 (-0.293) (Fig. 4) are estimated to be comparable to those derived (-0.285 and -0.284, respectively²) for BA.

Compound **1** represents the first di-substituted symmetric benzoic anhydride to be crystallographically characterised. However, it should be noted that a single crystal structure determination of a tri-substituted material, *viz.* 3,4,5-trimethoxybenzoic anhydride has appeared. This compound differs from **1** in the chirality of the crystal form [15] but the molecules also adapt the *syn*-conformational isomer in the solid-state.

3. Concluding remarks

The isolation and solid-state (X-ray) characterisation of piperonyl anhydride (1), the first di-substituted symmetric benzoic anhydride, has been carried out. The structure of 1 is shown to be in the *syn*-[1,2] conformation isomer (Figs. 3 and 4) with a pseudo-torsion angle about the anhydride functionality of 25.1°. The overall global structure and properties of various structural isomers of 1 and the parent benzoic acid itself have been further examined by the DFT level of theory (B3LYP 6-311G^{**}).

4. Experimental

4.1. General

General procedures and methods were carried out using standard bench top techniques similar to those described previously [12]. All reagents were purchased commercially and used as received. NMR spectra were recorded at room temperature on a Bruker Avance 400 NMR spectrometer using samples dissolved in chloroform-*d*. Coupling constant (*J*) values are reported in Hertz.

4.2. Isolation of 1

A mixture of 2,4,4-trimethyl-2-oxazoline (1.13 mL: 8.86 mmol), 2.5 mL of NEt₃ and 3.26 g of piperonyloyl chloride (17.7 mmol) were combined together in a 100 mL round-bottomed flask containing ~50 mL of MeCN. This mixture was heated to reflux temperature under an atmosphere of $N_2(g)$ for 20 h. After cooling the resulting orange solution to room temperature, the resulting solids (presumably [HNEt₃]Cl) [26b,27a] were filtered off and washed with a small amount of MeCN. The acetonitrile fractions were then combined and all volatile components were removed in vacuo. The residue was then extracted twice with CHCl₃ and water (~50 mL) and the organic fractions combined, dried (MgSO₄) and then evaporated to dryness by rotary evaporation. This procedure yielded a sticky, semi-solid brown-coloured mass (3.6 g). Analysis of this material *via* ¹H NMR indicated approximately a 45:55 ratio of the desired product (2) [28] and a second component 1. A sample of this crude material (\sim 0.8 g) was then separated by flash column chromatography (SiO₂; EtOAc/hexanes: 5/8) and the fastest eluting

² Although reference [16] details the unit cell and general crystal parameters for crystalline BA, no bond lengths or angles are reported.

³ A value of 5.0 Debye was previously calculated for the dipole moment of BA at the semi-empirical (AM1) level of theory [15]. The other two *syn*-isomers of 1, *i.e.*, *syn*-[1,1] and *syn*-[2,2], present calculated dipole moments of 4.32 and 5.44 Debye, respectively. (see Supplementary material). The aforementioned calculations [15] also yielded Mulliken charge values of -0.29 and -0.32, for O3 and O5 respectively of BA.

material ($R_f = 0.61$) was collected and re-crystallised from CHCl₃/ hexanes (bp 35–60 °C range) to yield approximately 80 mg of pure 1 in the form of pale yellow needles. These needles were deemed to be suitable for X-ray diffraction methods.

Yield: 10%; mp: 153–156 °C.

IR (KBr: cm⁻¹): 3128 (s, br), 2923 (m), 2853 (m), 1768 (m), 1707 (m), 1605 (m), 1503 (m), 1489 (m), 1444 (m), 1400 (vs), 1254 (m), 1192 (w), 1136 (w), 1114 (w), 1095 (m), 1029 (m), 909 (m), 812 (w), 767 (w), 744 (w), 714 (w), 621 (w).

¹*H* NMR (400 MHz) δ_{H} /ppm: 7.76 (dd, 1H, *J* = 8.3, 1.8, ArH), 7.54 (dd, 1H, *J* = 1.7, 0.3, ArH), 6.90 (d, 1H, *J* = 8.4, ArH), 6.10 (s, 2H, CH₂).

 $^{13}C\{^{1}H\}$ NMR (75 MHz) δ_{C}/ppm : 161.3, 153.4, 148.6, 127.1, 122.7, 110.1, 108.4, 102.2.

4.3. Single crystal X-ray structure determination of 1

X-ray diffraction data were recorded on a Nonius Kappa CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and the resulting data collection obtained using Collect [31]. All estimated standard deviations (esds), except the esd in the dihedral angle between two l.s. planes, are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. The cell refinement and data reduction was performed with Denzo-smn [32]. The structure solution employed sir-92 [33] and the structure refinement was carried out with shelxtl 6.1 [34]. The molecular graphics were obtained using platon [35] and the publication materials were generated utilising shelxtl 6.1 [34]. The refinement of F^2 is against ALL reflections. The weighted R-factor wR and GoFs are based on F^2 , conventional R-factors R are based on *F*, with *F* set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors (gt), etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and *R*-factors based on ALL data will be even larger.

4.4. Molecular calculations of 1

The gas phase molecular calculations of BA and **1** were carried out using the Spartan 8.0 (Wavefunction Inc., Irvine CA, 2008) suite of software programs.

Supplementary material

Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication No. ccdc 776757. Copies of these data can be obtained free of charge on application to ccdc, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article (*i.e.*, .cif file of **1** and files, in .mol2 format, containing the structures of BA and **1** derived from the DFT treatment of these materials) can be found, in the online version, at doi:10.1016/ j.molstruc.xxxx.xxx or requested directly from the authors.

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