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Study on H-bond patterns in phosphoric triamides having a P(O)NHC(O) skeleton, a *gauche* orientation of P(O) *vs* C(O) in new compounds

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ABSTRACT

The crystal and packing structures of new phosphoric triamides, in a rare *gauche* orientation of P(O) *versus* C(O), with the formula $(CCl_2HC(O)NH)X_2P(O)$, X = NC_4H_8 (**1**), $N(C_2H_5)_2$ (**2**), $N(CH_3)(C_6H_{11})$ (**3**) and $(CCl_2HC(O)NH)(Y)P(O)$, Y = $NHCH_2C(CH_3)_2CH_2NH$ (**4**) have been investigated. This article also reviews 91 similar structures deposited in the CSD aiming to classify hydrogen bond patterns in this category of phosphorus compounds. The present X-ray structural analysis shows that the H-bond pattern in the studied structures strongly depends on the conformation in the P(O)NHC(O) skeleton and the kind of amide linked to the P atom. The spectroscopic features ($^{31}P\{^1H\}$, ^1H and ^{13}C NMR, IR) of the new compounds have been investigated.

1. Introduction

Hydrogen bonds (HBs) are the most important directional intermolecular interactions which may affect the preference of a molecular conformation and arrangement [1]. Many efforts have been performed to classify HBs based on their strengths [2,3] and morphology [4–6]. Such considerations help to predict crystal structures based on molecular structures. However, this is not yet completely possible, but it leads to classify HB patterns in analogous compounds and to obtain empirical "rules" which are most useful for predicting hydrogen-bond patterns of systems with a limited number of functional groups [7]. In this area, HB patterns have been discussed for nitroanilines [7], diarylureas [7], amides [8], imides [8], diamides [8] and different co-crystals [8]. Now, we wish to organize the existing data related to a biologically important functional group, P(O)NHC(O), belonging to *N*-carbonyl phosphoric triamides (CPAs, $RC(O)NHP(O)[NR^1R^2]_2$) [9]. Some derivatives have been investigated structurally [10–64], the cif files of which have been used for studying and classifying hydrogen bond patterns in CPAs and evaluating the behavior of different parts of the molecule in relation to the hydrogen bonds. This paper attempts to study the collective behavior of HBs in the crystal packing of CPAs. Among the 91 crystal structures found in the Cambridge Structural Database (CSD version 5.31 (November 2009)) and recently published papers (Table 1), there are only 10 structures with a non-*anti* orientation of C=O *versus* P=O. Here, we report 4 new structures with a *gauche* orientation and classify the H-bond patterns affected by the conformation of the P(O)NHC(O) skeleton and the kind of amide substituents linked to the P atom.

2. Experimental

2.1. Spectroscopic measurements

^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to TMS and ^{31}P chemical shifts relative to 85% H_3PO_4 as the external standards. The field strengths for the acquisition of ^1H, ^{13}C and ^{31}P spectra were 500.13, 125.77 and 202.46 MHz, respectively. Infrared (IR) spectra were recorded on a Buck 500 scientific spectrometer using KBr discs.

2.2. X-ray measurements

Single colorless crystals of compounds **1–4** were selected and glued on glass fibers. Diffraction data were collected on an Oxford Diffraction KM4 four-circle goniometer equipped with a Sapphire CCD detector. The crystals to detector distance was 45.0 mm and graphite monochromated Mo Kα (λ = 0.71073 Å) X-radiation was employed in all measurements. The frame widths of 1° in ω, with exp. time between 8 and 60 s were used to acquire each frame for **1**, **2**, **3** and **4**. More than one hemisphere of three-dimensional data was collected in all measurements. The data were reduced using the Oxford Diffraction program CRYSALISPRO [65]. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz,

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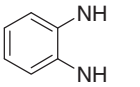
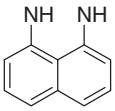
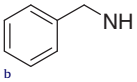
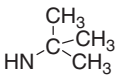
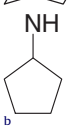
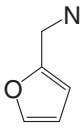
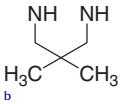
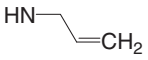
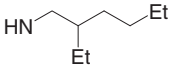
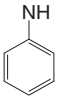
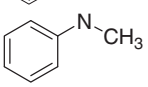
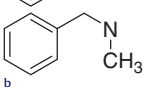
Table 1
[a]H-bond pattern for RC(O)NHP(O)[X]$_2$ compounds (X = Cl; XH = primary or secondary amine, alcohol; [XH]$_2$ = diamine); the point groups of H-bonded dimers are given in parenthesis as C_i for centrosymmetric and C_1 for non-centrosymmetric.

No	R	X/[X]$_2$ for diamine	O–P–N–C	Orientation	Packing	Refcode	Ref
1	4-F-C_6H_4		−177.6(3)	*anti*	1-D ladder	SAYJIM	[38]
2	CCl_3		−62.3(3)	*gauche*	2-D		[10]
3	C_6H_5		173.85(19)	*anti*	1-D chain	TOKXOH	[29]
4	4-F-C_6H_4	[b]	−179.04(11)	*anti*	1-D chain	KEBPOX	[39]
5	$CNCH_2$	[b]	164.06(17)	*anti*	1-D ladder	LOPBOI	[28]
6	CCl_3		177.7(3)	*anti*	1-D chain	PACNIR	[11]
7	3-NO_2-C_6H_4	[b]	177.6(1) 179.0(1) −180.0(1)	*anti*	Hexamer		[50]
8	C_6H_5	[b]	−174.8(2) 176.6(2)	*anti*	Two symmetrically independent 1-D chains	PACNEN	[11]
9	4-F-C_6H_4	[b]	−174.16(11)	*anti*	1-D chain	KEBPIR	[39]
10	NC_5H_4	[b]	[c]	*anti*	[c]		[64]
11	NC_5H_4	[b]	[c]	*anti*	[c]		[64]
12	4-NO_2-C_6H_4		170.69(13)	*anti*	1-D chain		[46]
13	CCl_3		−168.55(19)	*anti*	1-D chain	YIVPAV	[12]
14	4-Cl-C_6H_4	[b]	173.92(19)	*anti*	1-D chain	NOBHUI	[18]
15	4-CH_3-C_6H_4	[b]	166.55(12)	*anti*	1-D chain	YIVPEZ	[12]
16	$CNCH_2$		−163.85(16)	*anti*	1-D ladder	LOPCAV	[28]
17	$CHCl_2$		61.32(2)	*gauche*	1-D chain		[d]
18	4-F-C_6H_4	[b]	−57.2(2)	*gauche*	2-D		[40]
19	CCl_3		−169.9(3) −161.9(3) 161.1(3) 168.8(3)	*anti*	Two symmetrically independent 1-D chains		[13]
20	4-F-C_6H_4	[b]	166.2(1)	*anti*	1-D chain	TOKXEX	[29]
21	C_6H_5		178.5(4)	*anti*	1-D chain	GOKMEZ	[30]
22	CCl_3		174.8(6)	*anti*	[e]Dimer (C_i)	POKZAQ	[14]
23	CCl_3		174.9(4) 175.3(4)	*anti*	Dimer (C_1)		[15]
24	CCl_3		162.01(16)	*anti*	Dimer (C_i)	RAMBEN	[16]
25	$CHCl_2$	[b]	−178.16(17)	*anti*	Dimer (C_i)		[27]
26	C_6H_5	[b]	−165.2(2)	*anti*	Dimer (C_i)	RALZUA	[16]
27	4-F-C_6H_4	[b]	172.10(11)	*anti*	Dimer (C_i)	KEBPUD	[39]
28	4-Cl-C_6H_4	[b]	−171.90(14)	*anti*	Dimer (C_i)		[27]
29	4-Br-C_6H_4	[b]	−171.6(3)	*anti*	Dimer (C_i)	LIVWAP	[53]
30	CF_3	[b]	−176.2(2)	*anti*	Dimer (C_i)	WALRAD	[22]
31	2-F-C_6H_4	[b]	154.62(9)	*anti*	Dimer (C_i)	XIQZAZ	[42]
32	CCl_3		171.7(3) −151.1(4)	*anti*	Two symmetrically independent dimers (C_1)	VEHTAE	[17]
33	$CHCl_2$	[b]	56.2(3)	*gauche*	1-D chain		[d]

(*continued on next page*)