

The six-membered ring is not planar, the average and maximum deviations from the least-squares plane being 0.138 and 0.243 (9) Å respectively.

The magnitudes of the bond lengths and angles are also consistent with loss of aromatic character in this ring.

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Methyl 3,5-Di-*tert*-butyl-4-diisopropylamino-1H⁺-pyridazinium-6-phosphonate Dichloromethane Solvate, C₁₉H₃₆N₃O₃P·0.85 CH₂Cl₂: a Betaine Having a Nonplanar Pyridazinium Ring

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Abstract. $M_r = 457.69$, monoclinic, $P2_1/n$, $a = 12.491$ (4), $b = 17.206$ (7), $c = 12.532$ (5) Å, $\beta = 111.27$ (3)°, $V = 2510$ (1) Å³, $Z = 4$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.16$ cm⁻¹, $F(000) = 982.8$, $T = 297$ K, $R = 0.073$ for 3368 observed reflections. The molecule exists as a betaine, in which the acidic proton of the phosphonic acid group has been transferred to a nitrogen atom of the pyridazine ring. This ring is no longer planar but assumes a boat conformation; the bond pattern is best described as a 4-iminio-substituted 1,4-dihydropyridazine. In the crystal, the betaine forms a dimer held together by two N—H···O hydrogen bonds.

Introduction. The structure analysis was originally undertaken in order to confirm the substitution pattern of the heterocyclic ring. Inspection of molecular structure, then, revealed three noticeable features: (i) The molecule exists as a betaine, *i.e.* a proton transfer from the phosphonic acid function to a ring nitrogen has taken place. This was not unexpected, as 4-aminopyridazines are more basic than pyridines by more than one pK_a unit (Lenhart & Castle, 1973), and compounds like nicotinic acid (Gupta & Kumar, 1975)

or pyridine-3-sulfonic acid (Chandrasekhar, 1977) crystallize in the betaine form as well. (ii) The pyridazinium ring is not planar, but assumes a distinct boat form. (iii) The betaine forms a dimer by means of two P=O···H—N hydrogen bonds, a situation reminiscent of α -amino acids (Koetzle & Lehmann, 1976, and references cited therein) although, in the latter, such a dimer is only a building block in a three-dimensional network.

Experimental. The yellow crystals were a gift from M. Regitz and K. Feith; their preparation will be given elsewhere (Feith, 1985). Suitable crystals were obtained by crystallization from dichloromethane, but not all of the solvent could be removed without destroying the crystals. From an elemental analysis and the ¹H NMR spectrum, a CH₂Cl₂ content of 0.85 mol per mol of pyridazine was calculated. Crystal size 0.5 × 0.3 × 0.5 mm, Enraf-Nonius CAD-4 diffractometer, monochromatized Mo $K\alpha$ radiation. Cell constants from least-squares refinement of θ values of 23 reflections with $20.20 \leq 2\theta \leq 23.10^\circ$. No absorption correction. Data collection: θ range 2.0 to 25.0°, $\theta/2\theta$ scan, scan width (0.95 + 0.35tan θ)°, scan speed 1.42 to

4° min^{-1} , $h-14 \rightarrow 14$, $k 0 \rightarrow 20$, $l 0 \rightarrow 14$, $R_{\text{int}} = 0.057$ for equivalent reflections, 4420 independent reflections measured. Three monitor reflections (182, 611, 307) showed an intensity loss with an average of 6.5%, which was accounted for by linear correction. Structure solution by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), refinement by a full-matrix least-squares method on F . H atoms located from a difference Fourier map, some missing H atoms of methyl groups calculated, all included in structure-factor calculation only, with $B = 7.0 \text{ \AA}^2$ for methyl H atoms, otherwise B_{iso} of their heavy-atom neighbor. Occupancy factor of dichloromethane (0.85) not refined. 3370 reflections with $I > 2\sigma(I)$ considered observed and included in refinement, except for 040 and 222 (discarded because of high ΔF values, $F_o < F_c$). 262 variables, $R = 0.073$, $wR = 0.079$, $w = 1/[\sigma^2(F_o) + (0.014F_o)^2]$, $\Delta_{\text{max}}/\sigma = 0.23$, maximum residual electron density 0.69 e \AA^{-3} [0.9 \AA from Cl(1)]. Programs of Enraf-Nonius (1983) *SDP* used. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional and equivalent isotropic thermal parameters are given in Table 1, bond distances and angles in Table 2.* The structure of the molecule and the numbering scheme are given in Fig. 1.

Molecular structure

N-protonation of the heteroaromatic ring changes its geometry considerably, as compared to neutral pyridazines, e.g. pyridazine itself (Almenningen, Bjørnsen, Ottersen, Seip & Strand, 1977) or the fully substituted pyridazine (I) (Heydt, Eisenbarth, Feith, Urgast, Maas & Regitz, 1984). For the parent

* Lists of structure factors, anisotropic thermal parameters and coordinates of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42155 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

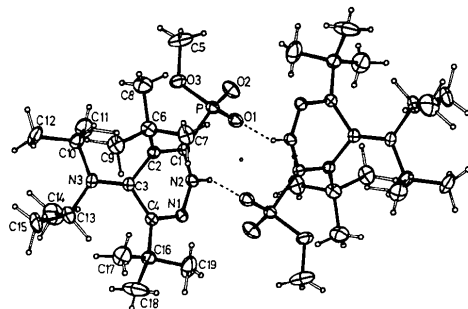


Fig. 1. ORTEP plot (Johnson, 1976). Two molecules, related by an inversion center, form a dimer held together by N-H...O bonds.

Table 1. Positional parameters and B_{eq} values with e.s.d.'s

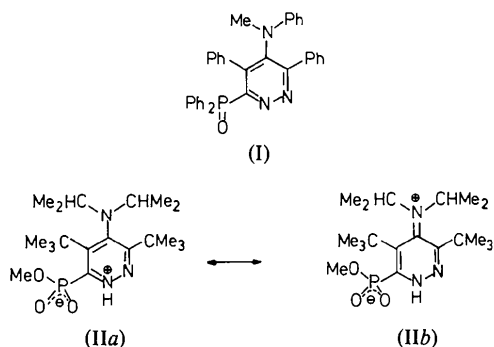
$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Cl(1)	0.6181 (2)	0.0807 (2)	0.1202 (2)	8.44 (6)
Cl(2)	0.5874 (3)	0.2200 (1)	0.2296 (2)	11.0 (1)
P	0.30999 (9)	0.03203 (7)	0.54382 (8)	2.35 (2)
O(1)	0.4305 (2)	0.0073 (2)	0.5750 (2)	3.01 (7)
O(2)	0.2236 (2)	-0.0224 (2)	0.5546 (2)	3.84 (7)
O(3)	0.3060 (2)	0.1127 (2)	0.6065 (2)	3.56 (7)
N(1)	0.3364 (3)	0.0730 (2)	0.2457 (3)	2.39 (8)
N(2)	0.3547 (3)	0.0652 (2)	0.3566 (3)	2.25 (7)
N(3)	0.1761 (3)	0.2375 (2)	0.2413 (3)	2.48 (8)
C(1)	0.2691 (3)	0.0722 (2)	0.3984 (3)	1.96 (8)
C(2)	0.1722 (3)	0.1131 (2)	0.3334 (3)	2.17 (9)
C(3)	0.1922 (3)	0.1621 (2)	0.2481 (3)	2.08 (9)
C(4)	0.2482 (3)	0.1159 (2)	0.1837 (3)	2.27 (9)
C(5)	0.2830 (4)	0.1132 (4)	0.7096 (4)	5.8 (1)
C(6)	0.0484 (3)	0.1012 (3)	0.3359 (4)	3.0 (1)
C(7)	0.0219 (4)	0.0141 (3)	0.3136 (4)	4.0 (1)
C(8)	0.0346 (4)	0.1230 (3)	0.4493 (4)	4.2 (1)
C(9)	-0.0432 (4)	0.1457 (3)	0.2366 (4)	3.7 (1)
C(10)	0.1569 (4)	0.2773 (3)	0.3397 (4)	3.1 (1)
C(11)	0.2720 (5)	0.2914 (3)	0.4365 (4)	4.7 (1)
C(12)	0.0848 (4)	0.3508 (3)	0.3074 (4)	4.6 (1)
C(13)	0.2021 (4)	0.2837 (3)	0.1524 (4)	3.7 (1)
C(14)	0.3033 (5)	0.3395 (3)	0.2027 (5)	6.0 (2)
C(15)	0.0962 (5)	0.3260 (3)	0.0693 (5)	5.7 (2)
C(16)	0.2070 (4)	0.1015 (3)	0.0535 (3)	3.2 (1)
C(17)	0.0879 (5)	0.1315 (3)	-0.0089 (4)	5.2 (1)
C(18)	0.2904 (5)	0.1391 (5)	0.0033 (4)	7.5 (2)
C(19)	0.2043 (6)	0.0130 (3)	0.0362 (5)	6.4 (2)
C(20)	0.6090 (5)	0.1210 (4)	0.2433 (5)	4.6 (2)

Table 2. Bond distances (\AA) and bond angles ($^\circ$) with e.s.d.'s

Cl(1)-C(20)	1.732 (7)	C(2)-C(3)	1.453 (6)
Cl(2)-C(20)	1.725 (7)	C(2)-C(6)	1.570 (6)
P-O(1)	1.475 (3)	C(3)-C(4)	1.476 (6)
P-O(2)	1.471 (3)	C(4)-C(16)	1.543 (5)
P-O(3)	1.604 (3)	C(6)-C(7)	1.538 (7)
P-C(1)	1.840 (4)	C(6)-C(8)	1.539 (7)
O(3)-C(5)	1.421 (7)	C(6)-C(9)	1.553 (6)
N(1)-N(2)	1.331 (4)	C(10)-C(11)	1.527 (6)
N(1)-C(4)	1.319 (5)	C(10)-C(12)	1.520 (7)
N(2)-C(1)	1.356 (6)	C(13)-C(14)	1.530 (7)
N(3)-C(3)	1.312 (5)	C(13)-C(15)	1.538 (7)
N(3)-C(10)	1.504 (6)	C(16)-C(17)	1.499 (7)
N(3)-C(13)	1.497 (6)	C(16)-C(18)	1.541 (9)
C(1)-C(2)	1.382 (5)	C(16)-C(19)	1.537 (7)
O(1)-P-O(2)	120.3 (2)	N(1)-C(4)-C(16)	114.8 (4)
O(1)-P-O(3)	109.3 (2)	C(3)-C(4)-C(16)	128.5 (3)
O(1)-P-C(1)	105.1 (2)	C(2)-C(6)-C(7)	105.8 (4)
O(2)-P-O(3)	110.6 (2)	C(2)-C(6)-C(8)	115.3 (3)
O(2)-P-C(1)	112.3 (2)	C(2)-C(6)-C(9)	111.4 (4)
O(3)-P-C(1)	96.5 (2)	C(7)-C(6)-C(8)	108.5 (4)
P-O(3)-C(5)	120.2 (3)	C(7)-C(6)-C(9)	106.6 (3)
N(2)-N(1)-C(4)	117.5 (4)	C(8)-C(6)-C(9)	108.8 (4)
N(1)-N(2)-C(1)	122.2 (3)	N(3)-C(10)-C(11)	109.9 (4)
C(3)-N(3)-C(10)	117.6 (4)	N(3)-C(10)-C(12)	114.5 (4)
C(3)-N(3)-C(13)	120.2 (4)	C(11)-C(10)-C(12)	112.0 (4)
C(10)-N(3)-C(13)	120.8 (3)	N(3)-C(13)-C(14)	113.3 (4)
P-C(1)-N(2)	112.0 (2)	N(3)-C(13)-C(15)	112.9 (4)
P-C(1)-C(2)	130.1 (3)	C(14)-C(13)-C(15)	111.1 (4)
N(2)-C(1)-C(2)	117.6 (4)	C(4)-C(16)-C(17)	112.5 (4)
C(1)-C(2)-C(3)	112.4 (4)	C(4)-C(16)-C(18)	110.4 (4)
C(1)-C(2)-C(6)	125.4 (4)	C(4)-C(16)-C(19)	106.9 (4)
C(3)-C(2)-C(6)	121.6 (3)	C(17)-C(16)-C(18)	109.5 (4)
N(3)-C(3)-C(2)	123.9 (4)	C(17)-C(16)-C(19)	107.5 (4)
N(3)-C(3)-C(4)	126.0 (4)	C(18)-C(16)-C(19)	110.0 (5)
C(2)-C(3)-C(4)	109.5 (3)	Cl(1)-C(20)-Cl(2)	111.4 (4)
N(1)-C(4)-C(3)	116.1 (3)		

pyridazine, the following bond lengths have been found by electron diffraction: N—N 1.330 (1), N—C_α 1.341 (2), C_α—C_β 1.393 (2), C_β—C_{β'} 1.375 (1) Å. The same bonding pattern was encountered in the 4-amino-substituted pyridazine (I), even though distances were up to 0.02 Å longer. In the title compound, only the N(1)—N(2) distance remains unchanged [1.331 (4) Å], but all other ring distances have changed in a manner which is expected if the bond state is mainly determined by resonance structure (IIb), *i.e.* a 4-iminio-substituted 1,4-dihydropyridazine, and less by (IIa). Specifically, the C(2)—C(3) [1.453 (6) Å] and C(3)—C(4) [1.476 (6) Å] distances are in the usual range of C_{sp²}—C_{sp²} single bonds, and the C—N bond lengths, N(1)—C(4) [1.319 (5) Å] and C(3)—N(3) [1.312 (5) Å] are quite close to the corresponding value for the *N,N*-dimethylisopropylideneiminium ion, Me₂C=N⁺Me₂ (1.302 Å) (Trefonas, Flurry, Majeste, Meyers & Copeland, 1966), which is considered to represent a true C=N⁺ double bond. In contrast, comparison of the structure of 4-dimethylaminopyridinium chloride (Chao, Schempp & Rosenstein, 1977) and 4-aminopyridine (Chao & Schempp, 1977) shows a much less pronounced contribution of the cross-conjugated resonance structure: The exocyclic C—N distance in the protonated molecule is 1.340 (3) Å, only 0.023 Å shorter than in the neutral molecule. For the title compound, on the other hand, the exocyclic C—N bond is about 0.1 Å shorter than in the neutral 4-amino-substituted pyridazine (I) (of course, the influence of different N-substitution may account partly for this difference).



Other than the heteroaromatic ring of 4-dimethylaminopyridinium chloride, the six-membered ring of the pyridazinium salt is no longer planar. A slightly twisted boat form is found, with N(2) and C(3) at the tips of this boat. The least-squares plane through C(1), C(2), N(1), C(4) [deviations: C(1) 0.019 (4), C(2) -0.019 (4), C(4) 0.020 (4), N(1) -0.020 (3) Å] forms dihedral angles of 21.0 (5)° with C(1)—N(1)—N(2) and 43.1 (5)° with C(2)—C(3)—C(4). The dialkylamino function, C(13)—N(3)—C(10), is tilted by 21.1 (5)° against C(4)—C(3)—C(2). This unusual conformation,

as well as some deviations of exocyclic bond lengths and angles from 'ideal' values (see Table 2), is certainly due to the heavy substitution pattern which requires minimization of steric strain, especially between *tert*-butyl and isopropyl groups, but also between the phosphonate function and the *tert*-butyl group at C(2) [torsion angle P—C(1)—C(2)—C(6) -33.4 (3)°].

Hydrogen bonding

Two molecules, symmetrically related by an inversion center, are held together by two N—H...O hydrogen bonds. The situation is depicted in Fig. 2. A phosphoryl oxygen serves as an acceptor of the hydrogen bond. Some other examples of intermolecular P=O...H—N hydrogen bonds are known (*e.g.* Hayden, Kim & Eriks, 1982, and references cited therein), which are clearly non-centered with O...N contacts between 2.71 and 2.98 Å. The hydrogen bond under consideration is non-centered as well, in agreement with its IR spectra, where only NH bands at 3410 and 3270 cm⁻¹ were found. In contrast, a dimer analogous to the structural moiety of Fig. 2, but with carboxylate instead of phosphonate (6-bromo-1,10-dioxo-1,2,9,10-tetrahydro-4,7-phenanthroline-3,8-dicarboxylic acid), is believed to have a very strong, asymmetric single-potential-minimum N...H...O bond according to its broad IR absorption, centered around 800 cm⁻¹ (Smith, Taylor, Vause & Waring, 1978).

Besides the intermolecular hydrogen bond, Fig. 2 also shows a rather short *intramolecular* H(N2)...O(1) contact (2.30 Å), which is close to the van der Waals distance (2.40 Å) and for which the angle N(2)—H(N2)—O(1) is much more bent than for the intermolecular hydrogen bond. Whether or not such a coordination should be considered a bifurcated hydrogen bond is open to debate (Taylor, Kennard & Versichel, 1984; Olovsson & Jönsson, 1976). Some authors argue that, if the system under consideration is planar [torsion angle O(1)—P—C(1)—N(2) 3.1 (2)°, H(N2) approximately in that plane], a close proximity between acceptor and hydrogen is imposed onto it, giving rise to a weak electronic interaction between both atoms, but not to a true hydrogen bond. The question, however, remains, as to what forces these atoms into a

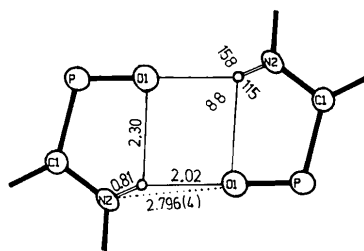


Fig. 2. Details of hydrogen bonding: distances (Å) and angles (°). The position of H(N2) has not been refined.

planar arrangement, as, in principle, free rotation around the C(1)—P bond is possible. It seems very likely, that not only interaction with the neighboring *tert*-butyl group and a maximum degree of intermolecular hydrogen bonding, but also the possibility of acquiring additional stabilization by the intramolecular H...O contact contribute to the final geometry.

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**[Methylenebis(*N,N'*-dimethylurea)]hydrogen(I) Trifluoromethanesulfonate,*
 $C_7H_{17}N_4O_2^+CF_3O_3S^-$: a Very Strong Intramolecular O...H...O Bond**

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Abstract. $M_r = 338.3$, triclinic, $P\bar{1}$, $a = 7.055$ (1), $b = 9.582$ (1), $c = 11.955$ (8) Å, $\alpha = 83.92$ (4), $\beta = 82.14$ (3), $\gamma = 70.36$ (1)°, $V = 752.5$ Å³, $Z = 2$, $D_x = 1.493$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.62$ cm⁻¹, $F(000) = 352$, $T = 297$ K, $R = 0.0528$ for 2160 observed reflections. A very short hydrogen bond connects the two carbonyl oxygen atoms of the diurea, so that an eight-membered ring is formed, O...O 2.420 (3) Å. The anion is associated with two cations by hydrogen bonds of the N—H...O type: N...O 2.908 (3) and 2.855 (3) Å.

Introduction. Several examples of intermolecularly proton-connected assemblies of two carbonyl units are

known and their structures have been determined, e.g. for urea (Zhang, Shao, Xu & Tang, 1981), acetamide (Groth, 1977; Muir & Speakman, 1979) or benzo-homotropone (Childs, Faggiani, Lock & Varadarajan, 1984). These systems belong to the HX_2^+ type (where X is a heteroatom). In contrast, most intramolecular hydrogen bonds between two carbonyl oxygen atoms, whose geometries have been investigated so far, belong to the HX_2^- type (Emsley, 1980; Olovsson & Jönsson, 1976). Apart from protonated bis(1,2-dihydro-1,5-dimethyl-3-oxo-2-phenyl-3H-pyrazol-4-yl)methane (Burschka, Akgun & Pindur, 1983), the title compound is the only example of an intramolecular hydrogen bond of the HX_2^+ type connecting two carbonyl groups. The structure of the former compound was, however, not completely refined, and no hydrogen atoms were localized. The intramolecular hydrogen bond, in that case, was indicated by an O...O contact of 2.47 (1) Å.

* (4,6-Dimethyl-2,4,6,8-tetraaza-3,7-nonanedione)hydrogen(I) trifluoromethanesulfonate.