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The molecular structure of dichloro(dimethylamino)phosphine

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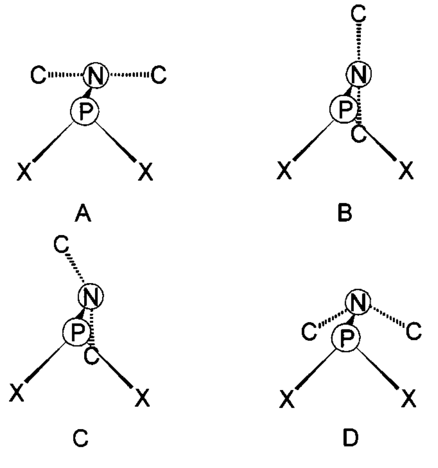
The solid state structure of the low-melting compound $Cl_2P–NMe_2$ was determined by X-ray diffraction using an *in situ* grown single crystal. Two independent molecules in the asymmetric unit have very similar geometries with planar co-ordination at their nitrogen atoms and the C_2NP unit almost coinciding with the approximate molecular plane of symmetry. According to *ab initio* calculations up to the MP2/6-311G** level of theory the structure in the solid state corresponds to a transition state of inversion of the nitrogen pyramid, which is about 3.1 kJ mol^{-1} higher in energy than the ground state. The calculated ground state is of C_1 symmetry with a *gauche* arrangement of the NMe_2 group. Both conformations of $Cl_2P–NMe_2$ are at variance to that determined by gas-phase electron diffraction in 1966, with a planar Me_2NP group being oriented perpendicular to the plane of symmetry. The calculations predict the latter structure not to be a stationary point on the potential hypersurface. The preference for the C_s structure of $Cl_2P–NMe_2$ in the crystal can be rationalised by the molecular dipole moments which are larger for the C_s structure than for the C_1 ground state. The results are discussed in comparison to the structure of $F_2P–NMe_2$ which was determined earlier in the gaseous and solid state, also with different geometries. New *ab initio* calculations for $F_2P–NMe_2$ are provided favouring C_1 symmetry, but showing the molecule to have a very small barrier to inversion of the nitrogen centre if any.

Introduction

Recently we have reported the molecular structures of compounds containing $P(NR_2)_3$ units, which have one pyramidal and two planar co-ordination geometries at the nitrogen centres.[1] This phenomenon seems to be inherent in the chemistry of $P(NR_2)_3$ units and has now also been shown to be operative in $E(NR_2)_3$ units with E = As or Sb.[2] As nitrogen and chlorine have similar electronegativities, it seemed desirable to compare these structures to those of the type $Cl_2E–NMe_2$. A gas-phase structure determination for $Cl_2P–NMe_2$ has already been described.[3] In this study many possible conformations were discussed, but the one which was favoured is not convincing with respect to today's background of experimental and theoretical knowledge. This structure describes $Cl_2P–NMe_2$ as C_s symmetric, with a planar C_2NP unit oriented perpendicular to the molecular plane of symmetry (structure A).



X = F, Cl

Much effort was spent in determining the structure of the closely related compound, $F_2P–NMe_2$. As in the case of $Cl_2P–NMe_2$, the gas-phase electron diffraction (GED) data of $F_2P–NMe_2$ were refined under the assumption of local C_s symmetry for the Me_2N group, but the C_2NP unit in this compound was found to be slightly non-planar and placed in an asymmetric *gauche* conformation (C). A more recent microwave spectroscopy study on $F_2P–NMe_2$ described the C_2NP unit as being planar and coinciding exactly with the molecular plane of symmetry (B). This C_s structure is also consistent with that adopted by $F_2P–NMe_2$ in the crystal.[4]

In order to resolve the present contradiction in the literature concerning the differences between the molecular structures of $Cl_2P–NMe_2$ (and $F_2P–NMe_2$), we have now determined its crystal structure at low temperature and performed *ab initio* calculations up to the MP2/6-311G** level of theory. We wish to focus the discussion on the question of whether the nitrogen co-ordination geometry in these molecules is planar and on the contradictory statements about the relative conformation of the X_2P and NMe_2 groups.

Results and discussion

A single crystal of $Cl_2P–NMe_2$ was grown by microscale zone refinement in the cryostream of the diffractometer. The lowest possible temperature for data collection of this compound was found to be −130 °C, as the crystal quality rapidly decreased upon further cooling. The crystal under examination was monoclinic and belonged to the space group $P2_1/c$ with $Z = 8$ and two independent molecules in the asymmetric unit.

The geometries of these two molecules (Fig. 1) were found to be very similar, *i.e.* there is no significant difference in most of the corresponding parameter values (see Table 1). This and the absence of pronounced intermolecular interactions is a good indication of molecular geometries which are not distorted by lattice forces and thus comparable to the results of gas-phase measurements and *ab initio* calculations.

In the crystal the molecules of $Cl_2P–NMe_2$ have almost a mirror plane of symmetry passing through their $P–NC_2$ units, although there is no exact crystallographic symmetry imposed on the molecules geometries. The deviation of the C_2NP unit from a planar arrangement is marginal, as can be seen from the values of the dihedral angles C(1)NPC(2), which are 1.3 and

Table 1 Selected geometrical parameter values (Å,°) of $Cl_2P–NMe_2$ and $F_2P–NMe_2$ for comparison

	$Cl_2P–NMe_2$ (X = Cl)					$F_2P–NMe_2$ (X = F)				
	XRD		MP2/6-311**		GED[3] (C_s)	GED[4] (C_1)	MW[5] (C_s)	XRD[6] (C_s)	MP2/6-311G**	
	Molecule 1	Molecule 2	GS (C_1)	TS (C_s)					GS (C_1)	TS (C_s)
P–N	1.632(2)	1.631(2)	1.669	1.653	1.694(30)	1.648(8)	1.6571(6)	1.628(5)	1.658	1.653
P–X(1)	2.092(1)	2.095(1)	2.122	2.101	2.083(5)	1.589(3)	1.5945(7)	1.610(4)	1.626	1.621
P–X(2)	2.091(1)	2.095(1)	2.072	*a*	*a*	*a*	*a*	*a*	1.616	*a*
N–C(1)	1.454(3)	1.460(3)	1.462	1.458	1.470(20)	1.448(6)	1.4503(3)	1.485(8)	1.460	1.458
N–C(2)	1.458(3)	1.457(3)	1.467	1.460	*b*	*b*	*b*	1.460(9)	1.457	1.455
X–P–X	94.7(1)	94.7(1)	98.7	97.4	98(1)	99(3)	93.49(5)	91.5(3)	93.793.2	
N–P–X(1)	103.4(1)	102.7(1)	103.7	102.2	100(1)	97(4)	100.70(3)	101.6(2)	102.5	100.7
N–P–X(2)	103.0(1)	103.0(1)	99.9	*a*	*a*	*a*	*a*	*a*	98.7	*a*
P–N–C(1)	126.8(2)	126.4(2)	123.2	126.5	120(2)	118.3(6)	124.05(5)	123.7(5)	122.6	123.7
P–N–C(2)	118.0(2)	118.7(2)	114.0	118.6	*c*	*c*	119.73(2)	120.4(5)	118.9	120.5
C–N–C	115.1(2)	114.8(2)	112.5	114.8	120(2)	111.8(15)	116.22	115.9(6)	114.5	115.8
τC(1)NPX(1)	−52.0(2)	−44.7(2)	54.0	50.3		*d*	47.83(3)	47.0	−49.8	47.7
τC(1)NPX(2)	46.1(2)	53.3(2)	−47.5	*a*		*d*	*a*	*a*	46.0	*a*
τC(2)NPX(1)	129.3(2)	132.3(2)	94.7	50.3						
τC(2)NPX(2)	−132.3(2)	−129.8(2)	−163.7	*a*						

[a] Symmetry equivalent. [b] Assumed to be equal to N–C(1). [c] Assumed to be equal to P–N–C(1). [d] 86(2)°, this dihedral angle is defined as the angle between the planes bisecting the angles F–P–F and C–N–C.

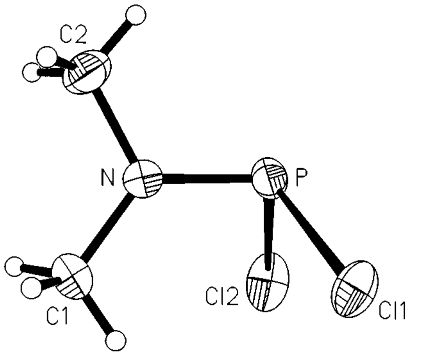


Fig 1. Molecular structure of $Cl_2P–NMe_2$ in the crystal as determined by low-temperature X-ray crystallography. Only one of the two independent molecules in the asymmetric unit is shown.

3.0° for the two molecules. The conformation in the solid state is such that the NC_2 units of the dimethylamino groups coincide with the plane bisecting the PCl_2 angle (conformation B). This means that the Me_2N group in $Cl_2P–NMe_2$ adopts a conformation which is perpendicular to that of the geometry derived from the GED data in 1966 (conformation A).[3]

The P–Cl bond lengths in the crystal are determined to be very similar to those obtained by the GED study, although natural differences resulting from the application of different physical methods are not taken into consideration. The P–N and N–C bond lengths are both shorter than their corresponding values in the gas phase, however, the large standard deviations of the GED parameters attribute no significance to those differences. The P–N bond length in crystalline $Cl_2P–NMe_2$ is the same as in the fluorine analogue $F_2P–NMe_2$, which has been considered as short and attributed to π-bonding,[6] based on the planar nitrogen centre.

The N–P–Cl angles are only about 3° larger in the solid state than in the gas phase and the Cl–P–Cl angles are smaller in the solid state by the same magnitude. The P–N–C angles were assumed to be equal in the GED refinement, a consequence of a molecular symmetry constraint. In the solid state, however, both P–N–C angles are significantly different: on average over both molecules the angle P–N–C(1) is 8.4° larger than the angle P–N-C(2). This can be attributed to a repulsion between C(1) and the two chlorine atoms.

The observed solid state geometry of $Cl_2P–NMe_2$ is very similar to that of $F_2P–NMe_2$. Moreover, two different P–N–C angles have also been found in a microwave spectroscopy study on $F_2P–NMe_2$. An older GED structure, which assigned a *gauche* structure of C_1 symmetry to $F_2P–NMe_2$, has also been refined under the assumption of two equal P–N–C angles.

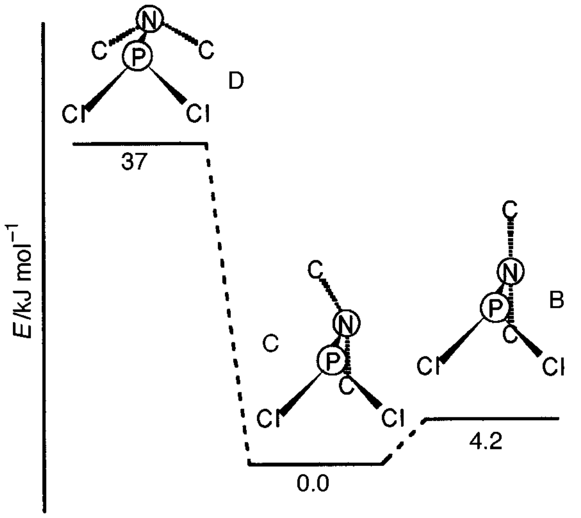


Fig. 2 Calculated energies (MP2/6-311G**) of different conformations of $Cl_2P–NMe_2$.

We performed *ab initio* calculations up to the MP2/6-311G** level of symmetry on $Cl_2P–NMe_2$, whereby a single minimum on the potential hypersurface was located corresponding to conformation C. Conformation B, which is obtained by application of a symmetry constraint (C_s) does not correspond to a minimum, but a transition state to inversion of the nitrogen pyramid, as was shown by the occurrence of one imaginary frequency in a frequency calculation at the MP2/6-31G* level of theory. This is surprising as this conformation is adopted by both independent molecules in the crystal lattice. The barrier to inversion is predicted to be 4.2 kJ mol^{-1} at MP2/6-311G** and to only 3.1 kJ mol^{-1} if zero point vibrational energy (calculated at MP2/6-31G*) is taken into consideration (see Fig. 2). This is low compared to kT, which is 1.2 kJ mol^{-1} at the temperature of the X-ray diffraction experiment. The close similarity of the crystallographic results and the calculated transition-state geometry manifests itself by the good agreement between the bond angles (see Table 1), which all fall within a range of 1° of one another. Such a finding seems not completely uncommon and quite recently we have reported two other examples of crystal structures, which are close to transition-state geometries

($H_3SiOCHMe_2$[7] and $Me_3P{=}CH_2$[8]). Distortion energies of up to *ca.* 6 kJ mol^{-1} can be provided by lattice forces without occurrence of short intermolecular van der Waals contacts.

A simpler explanation for the observed solid state structure is based on the molecular dipole moment. The dipole moment of the calculated C_s geometry is predicted to be 4.11 D, whereas the dipole moment of the C_1 structure is only 3.75 D. Because of the general tendency of molecules to increase their dipole moment upon incorporation into a crystal lattice,[9] this is probably the driving force for the molecules to adopt C_s symmetry in the crystal.

The geometry of the calculated ground state is more different from the solid state structure than the transition-state geometry. This becomes obvious by comparing the angles P–N–C(1), P–N–C(2), C–N–C, N–P–Cl(1) and N–P–Cl(2), whereby deviations between experiment and theory are up to 3° and even larger deviations occur in the torsion angles.

In the calculations a conformation of type A corresponded neither to a minimum nor a transition state. However, a conformation D, with the nitrogen co-ordination deviating from planarity was found to constitute a transition state for the rotation about the P–N axis (C_s constrained geometry, one imaginary frequency at MP2/6-31G*). The barrier height for this rotation is predicted to be 37 kJ mol^{-1}, meaning that this conformation does not contribute to an averaged gas-phase structure.

It is also worth mentioning that the P–N bond length of the calculated C_1 structure is 0.016 Å longer than in the C_s structure, which corresponds to the calculated and observed different P–N bond lengths in $P(NMe_2)_3$ and $H_2C{=}P(NMe_2)_3$ with their longer P–N bonds connecting phosphorus to pyramidal nitrogen centres.[1]

The prediction of a non-planar structure for $Cl_2P–NMe_2$ led us to consider again the structures suggested for the related $F_2P–NMe_2$ and so we performed *ab initio* calculations up to MP2/6-311G** on $F_2P–NMe_2$. In essence these gave the same results as for the chlorine analogue with conformation C as the only stable minimum on the potential hyper surface. However, taking electron correlation into account in these calculations is crucial, as simple SCF calculations up to SCF/6-311G** predict the C_s structure to be the minimum. The minimum at MP2/6-311G** is only 0.5 kJ mol^{-1} lower in energy than the transition state and if the vibrational zero point energy corrections calculated at the MP2/6-31G* level are taken into account this barrier is only 0.1 kJ mol^{-1}, *i.e.* within the accuracy of such calculations we cannot say whether there is really a barrier or not.

This would mean that, despite the unjustified constraint of equal P–N–C angles and C–N bond lengths, the refinement of the gas-phase electron diffraction data by Holywell and Rankin[4] is in agreement with the calculations of the C_1 structure, whereas the C_s constrained structure derived from microwave data is in good agreement with the C_s constrained *ab initio* optimisation. However, as the calculated barrier is only low or does not exist at all, care is suggested with the interpretation of the theoretical and experimental results. In this case the time scale of observation becomes important; microwave spectroscopy which operates on a slower time scale observes the average molecular structure, which is C_s, whereas the faster electron diffraction method “sees” the conformation of highest probability C_1. We can conclude that the molecule has a very floppy co-ordination geometry at the nitrogen centre and the question arises whether one should further search for an absolute minimum, which is of very limited meaning in reality.

The preference for a C_s geometry in the solid state of $F_2P–NMe_2$ seems to be of the same origin as in $Cl_2P–NMe_2$. The difference between the dipole moments of C_s (3.48 D) and C_1 (3.38 D) is smaller than that in the chlorine analogue, but so is the barrier to be overcome to adopt a C_s arrangement.

However, at this stage it can be concluded almost with certainty that the conformation of $Cl_2P–NMe_2$ favoured from the GED data in 1966 is unrealistic.[3] It is probably the non-valid assumption of equal P–N–C angles which led the refinement of the GED data of $Cl_2P–NMe_2$ to converge with a unlikely high-energy conformation. With the introduction of additional experimental observations into the refinement or with *ab initio* restrained GED data analysis it should be possible to retrieve the correct gas-phase structure of $Cl_2P–NMe_2$ from the diffraction intensities.

The results obtained for $F_2P–NMe_2$ suggest that further improvement in the level of theoretical treatment of $Cl_2P–NMe_2$ is necessary for a decision whether the solid state molecular structure really corresponds to a transition state of inversion or, like in the fluorine analogue, is one point within a very shallow potential. Such calculations, however, are beyond our current resources.

Experimental

$Cl_2P–NMe_2$ was prepared by a literature method.[10]

Crystal structure determination

A single crystal was grown *in situ* by slowly cooling the melt in a sealed thin walled Duran-capillary after generation of a suitable seed crystal from −64 to −67 °C. $C_2H_6Cl_2PN$, $M = 145.95$, monoclinic, space group $P2_1/c$, $a = 14.669(3)$, $b = 5.8891(5)$, $c = 14.785(4)$ Å, $\beta = 101.17(1)°$, $U = 1253.0(4)$ Å^3 at 143(2) K, $Z = 8$, μ(Mo-Kα) = 1.157 mm^{-1}. Data were collected at 143(2) K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα-radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were determined by non-linear least-squares refinement of 88 accurately centred reflections (θ range 19–24°). 2816 Reflections were collected with $1.5 < 2\theta < 54°$ using ω scans and a scan width of 1.8°. Equivalent reflections were merged to give 2714 independent reflections ($R_{int} = 0.0132$) which were used in the refinement. Crystal stability was monitored by three check reflections every 60 min and no intensity decrease occurred. No absorption correction was applied. The structure solution was done by direct methods;[11] the refinement with SHELXL 93.[12] Non-H atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms were located in Fourier-difference maps and refined isotropically. With 157 parameters refining, the refinement converged with $R_1 = 0.0321$ for 2714 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.0843$ for all data; $w = 1/[\sigma^2(F_o^2) + (0.0509\,P)^2 + 0.38\,P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$. The residual electron density was 0.57 and −0.47 e Å^{-3}.

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Ab initio calculations

Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[13] Geometry optimizations and vibrational frequency calculations were performed from analytic first- and second-derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G*,[14–16] 6-31G*[17–19] and 6-311G**[20,21] basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. Frequency calculations on all optimised geometries were carried out up to the MP2/6-31G* level of theory.

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