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Structure and electronic structure of $[(CF_3)_2PN]_2NVCl_2$, a molecule involving a planar six-membered ring (N_3P_2V)

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Summary. The SCF method is applied to determine the (gas phase) structure of $[(CF_3)_2PN]_2NVCl_2$, which agrees with the solid-state X-ray structure within typical errors of 2 pm and 2° in bond distances and angles. The electronic structure of atoms forming the ring is best described in terms of divalent N^- and tetravalent P^+ with appreciable declocalization of nitrogen lone pairs into low-lying empty orbitals of neighbouring atoms P and V. No evidence for aromaticity of the ring system is found.

Key words: $[(CF_3)_2PN]_2NVCl_2$ – SCF method

1. Introduction

The molecule investigated theoretically in this work has been synthesized and its structure determined by Roesky et al. [1]. It is a typical representative of a class of compounds [2] showing a planar or almost planar six-membered ring system involving one or two transition-metal atoms besides main row atoms, e.g. N and P.

The (near) planarity of the ring system quite naturally leads to the question of aromaticity of these molecules. In the present work we report and discuss the results of ab initio SCF calculations for $[(CF_3)_2PN]_2NVCl_2$ **1**, shown in Fig. 1. Our aim is mainly to interpret and elucidate the electronic structure. We have chosen **1** for this purpose since the molecule has (almost) the relatively high C_{2v} symmetry which facilitates a theoretical treatment.

In the following section we specify details of our computations, especially basis sets. In Sect. 3 we report the results for the molecular equilibrium structure as determined computationally on the SCF level in comparison with the experimental results from X-ray diffraction measurements. The electronic structure will be discussed in Sect. 4.

2. Details of computation

All calculations have been carried out with the program system TURBOMOLE [3] on a workstation computer HP 835. We have assumed C_{2v} molecular

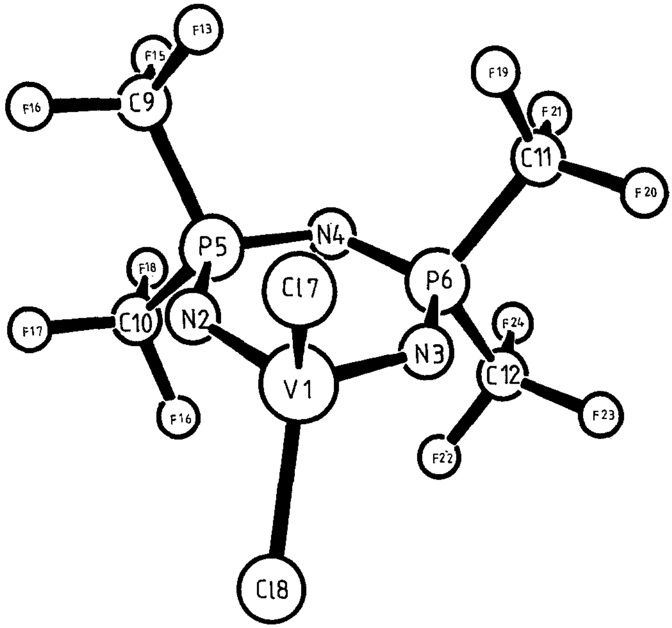


Fig. 1. Structure of **1**. $[(CF_3)_2PN]_2NVCl_2$

symmetry (a slight distortion to C_2 is found in the solid) but all remaining structure constants have been optimized on the basis of analytical gradients with a new geometry relaxation procedure [4].

The basis set of contracted Gauss type orbitals (CGTO) employed in the present work is defined in the following way:

N, C, F: a *DZ* basis *(8,4)/[4,2]* [5a] augmented by a *d* set for N with $\eta_d = 0.8$.

P, Cl: a split valence polarization basis (*SVP*) *(9,6,1)/[4,3,1]*, with $\eta_d = 0.34$ (P), 0.32 (Cl). The *sp* basis sets are derived from Huzinaga's "single zeta" basis *(432/42)* [5b] by decontracting the two primitives in the valence shell. This *SVP* basis has proved useful in a series of test calculations and usually gives slightly too short (0 to 2 pm) equilibrium distances as compared with experiment [6].

V: the basis set *(11,8,4)/[5,4,2]* was derived from Huzinaga's *(4333/43/4)* basis [5b] by decontracting the 3*s*, 3*p*, and 3*d* AOs to *DZ* by taking the most diffuse function out of the contraction. We then performed trial calculations for VCl_5, in D_{3h} symmetry, since this was considered a typical V^V compound. In these calculations we reoptimized the 3*d* type functions and determined the basis functions for the 4*s* and 4*p* AOs. This procedure lead to the basis described in Table 1.

Since VCl_5 is not known we cannot compare with experiment. For $TiCl_4$ (T_d) we have followed the very same procedure as for VCl_5. The basis set corresponding to the *V* basis (Table 1) lead to a TiCl distance of 218.4 pm (in connection with the *SVP* basis for Cl) which compares very well with experiment, TiCl = 219 pm [7].

The basis set described above is of only *DZ* type for the CF_3 groups and should lead to CF distances slightly larger than experiment. We are mainly interested in the ring system which is not directly influenced by the CF_3 groups, their most important effect results from a relatively high electronegativity which

Table 1. Specification of the V basis set as explained in the text[a]

Type	Exponent	Coefficient
s	7484.9750	.01759090
	1128.9149	.12301000
	255.66099	.44322549
	68.605402	.55050249
	102.77724	−.10466159
	11.024561	.62917076
	4.5135045	.44204467
		$\alpha = 1.039$
	7.7419278	−.35783056
	1.2337876	1.1604129
	.60000000	1.0000000
	.10000000	1.0000000
p	288.90480	.02984509
	67.234901	.18776639
	20.466783	.50623468
	6.8019129	.45411238
		$\alpha = 1.003$
	2.7909580	.38446539
	1.0582080	.67784186
	.39633561	1.0000000
	.07600000	1.0000000
d		$\alpha = 1.060$
	16.017249	.08624805
	4.1537439	.38064206
	1.2424358	.71222477
	.39000000	1.0000000

[a] α denotes the scaling factor of the original CGTO [5b]

draws electrons from P, and this effect was considered to be sufficiently well described by a *DZ* basis.

The structure determination was repeated with a partially extended basis set for N, P, Cl [5a]:

N: *(9,5,1)/[5,3,1]*

P, Cl: *(11,7,1)/[6,4,1]*.

This extended basis only leads to the expected slight shortening of some bond distances as will be reported in the next section. This implies that the smaller basis has no significant shortcomings as far as the atoms N, P, Cl are concerned. Following the suggestion of an (unknown) referee we also added a diffuse *d* GTO for V with exponent 0.15. This did not lead to any appreciable change of results (less than 1 pm in distances and less than 0.1 in atomic charges).

3. Comparison of experimental and computed structure

A complete structure optimization (within assumed C_{2v} symmetry) has been performed as a test of the appropriateness of the method used. Too large deviations between computed and measured structure constants would indicate shortcomings of the computed molecular electronic structure, which would jeopardize conclusions.

The comparison of present with X-ray data indicated a large deviation in the ∢ClVCl: 119.1° [1] vs 112.6° (this work). In an attempt to discuss this discrepancy, e.g. as a possible result of packing effects, we obtained the original data [8]. This uncovered a misprint in the ClVCl angle in Ref. [1], which should have been 111.9° instead of 119.1°. We are aware of the particular difficulties with this structure determination. Compound **1** is volatile but the desirable cooling below −80 °C was not possible since **1** undergoes a phase transition at lower temperatures. For this reason we report the detailed comparison in Table 2 which may serve as mutually supporting evidence of the reliability of experiment and theory. In Table 2 we give the structure data obtained from X-ray diffraction where necessary with corrections for large amplitude motions (especially librations). Note that only part of the uncorrected data – but no corrected data – was known to us during the calculations, the structure determinations were thus carried out independently, i.e. double blind.

SCF calculations employing *SVP* or *DZP* basis sets typically underestimate equilibrium distances by 1–3 pm. This trend is also reflected by the data in Table

Table 2. Comparison of the structure constants, in pm and degrees, of **1** as obtained from X-ray diffraction and present SCF calculations[a]

	X-ray[b]	SCF[c]
VN2	172.0	168.5
N2P5	161.3	160.4
N4P5	159.5	159.2
VCl	216.0 (218)	215.8
P5C10	190.1	186.6
P5C9	187.6	186.6
CF(av)	130 (134)	135.7
N2VN3	104.2	103.9
N2P5N4	118.1	118.6
P5N4P6	121.3	119.4
VN2P5	129.0	129.7
ClVCl	111.9	112.6
N2P5C(av)	108.5	108.4
N4P5C(av)	108.3	108.3
N2VCl(av)	110.1	110.0
PCF(av)	109.7	110.6

[a] atoms labelled as in Fig. 1 if confusion is possible. Average values are indicated by "(av)"

[b] Ref. [1], values corrected for large amplitude motions are given in parentheses if the effect of corrections exceeds 1 pm [8]

[c] basis set as described in text, C_{2v} symmetry assumed

2: the present SCF distances are typically 1 to 2 pm too short. An exception is the VN distance which is 3.5 pm too short. Considering the difficulties encountered in the theoretical description of transition metal compounds this is an acceptable error. Since a *DZ* basis was used for C and F we expect the CF distance to be computed a little too long. This is exactly what is found: computed CF distances vary between 135.6 and 135.9 pm, the corrected average CF distance is 134(3) pm [8]. The uncorrected CF distances (from X-ray diffraction) vary from 126.9 to 131.4 pm, with an average of 130 pm. The pronounced effect of large amplitude corrections no doubt is due to almost free rotation of CF_3 groups.

The SCF method further yields equilibrium angles with typical errors of 1° to 2°, and this is again reflected by the data in Table 2. Considering the difficulties in the evaluation of X-ray diffraction data and the errors of the SCF approximation it can be stated that theory and experiment agree within expected errors.

The more extended basis set mentioned above leads to a slight shortening in computed PN and PC distances (by 1 pm) and in the VCl distance (by 1.7 pm), the remaining distances differ by less than 1 pm, and angles by about 1°.

4. Characterization of the electronic structure

A convenient shorthand characterization of molecular electronic structures is provided by population analyses which yield measures of ionicity of bonding – by means of atomic charges – and of covalent contributions to bonding – by means of, e.g., shared electron numbers (SEN). Since atomic charges and individual bond strength (bond energies) are not measurable quantities, various proposals to extract corresponding quantities are necessarily arbitrary to some extent. We have applied the Mulliken population analysis [9] (MPA) and the population analysis based on occupation numbers as proposed by Davidson [10] and Roby [11], in the version described in Ref. [12].

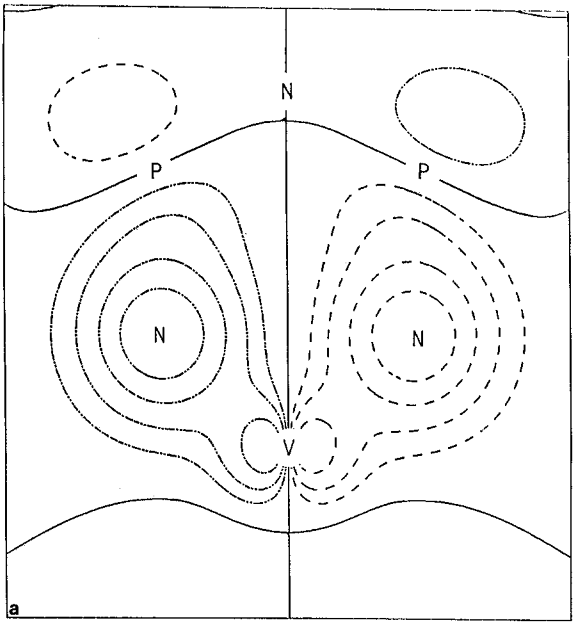
The net atomic charges obtained from the MPA and the population analysis based on occupation numbers are collected in Table 3. The results are relatively

Table 3. Computed atomic net charges according to the Mulliken population analysis (MPA) and the analysis based on occupation numbers (RD)[a]

	MPA	RD
V	1.81	2.23
N2	−0.86	−0.96
N4	−0.69	−0.81
P	0.77	0.99
Cl	−0.43	−0.57
C	0.94	0.79
F[b]	−0.32	−0.29

[a] atoms labelled as in Fig. 1. In the population analysis [12] we have employed 5 MAOs for C, N, F, 9 MAOs for P, Cl, and 14 MAOs for $V\,(1s-3d)$

[b] average value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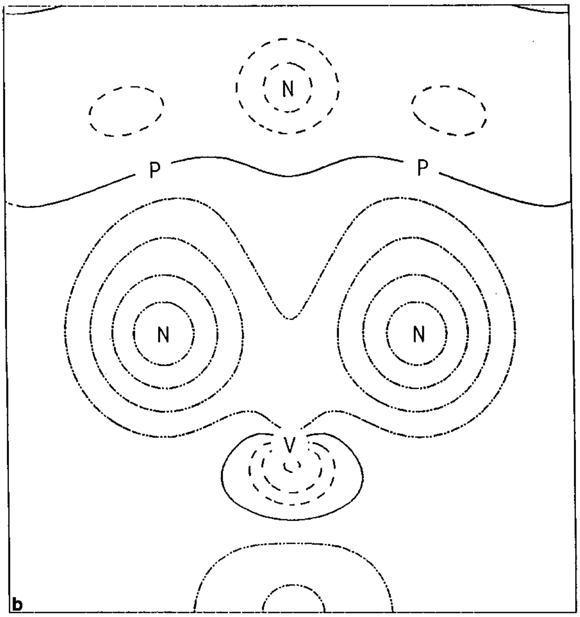
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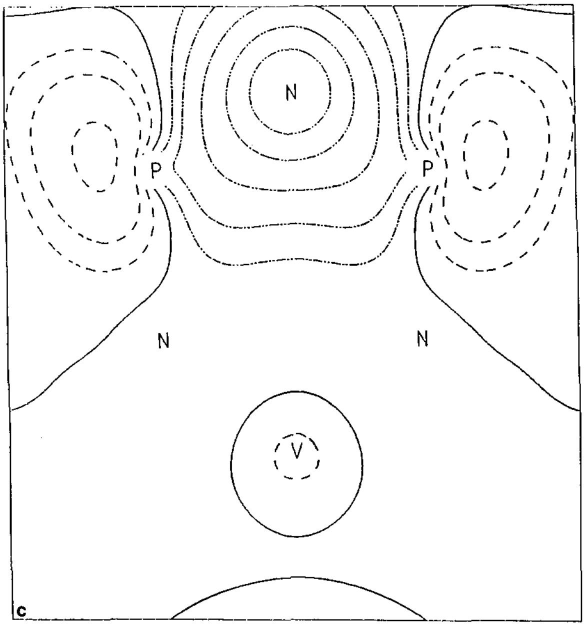

Fig. 2a–c. Contour diagrams of the MOs of **1**, which arise from nitrogen $2p\pi$ AOs. The plane shown is 0.5 a.u. (26 pm) above the VNP plane. Lines plotted correspond to 0 (*solid lines*), ±0.01, ±0.02, ±0.04, ±0.08, ±0.16, ±0.32 a.u. **a** MO $21a_2$, $\varepsilon = -12.7$ eV (HOMO) **b** MO $29b_2$, $\varepsilon = -12.8$ eV (2nd HOMO). **c** MO $28b_2$, $\varepsilon = -14.1$ eV

clear cut, i.e., with uncertainties of about 15% we get the following atomic charges q:

$$\mathrm{V}: q \approx 2$$
$$\mathrm{N2, N3}: q \approx -0.9$$
$$\mathrm{N4}: q \approx -0.75$$
$$\mathrm{P}: q \approx 0.85$$
$$\mathrm{Cl}: q \approx -0.5$$
$$\mathrm{C}: q \approx 0.8$$
$$\mathrm{F}: q \approx -0.3$$

These results suggest that as a zeroth-order approximation for the ring atoms one can start from tetravalent P^+ and divalent N^- atomic structures. A similar state of affairs has been found for other PN ring systems [13]. Vanadium – although formally V^V – is far from being d^0 with a formal charge $q = 5$. The MPA yields (total) vanadium gross occupations corresponding to $s^{6.1}p^{12.5}d^{2.6}$, indicating small contributions of 4s and 4p type AOs of 0.1 and 0.5 electrons respectively, but a considerable 3d participation. Consequently we have included only the 3d AOs (but not the 4s and 4p AOs) in the population analysis based on occupation numbers. (An inclusion of 4s and 4p AOs in this procedure reduces the unassigned charge only by 0.05 electrons, which also implies a negligible contribution to the molecular electronic structure.)

The contributions of 3d type orbitals of V give rise to appreciable covalent contributions to the VN and, to a lesser extent, also to the VCl bonds. This conclusion emerges from the SENs: SEN(VN) = 0.7 and SEN(VCl) = 0.3. We note for comparison that a covalent σ bond corresponds to SEN ≈ 1.4 and a covalent π bond to a contribution SEN ≈ 0.8.

The phosphorous atoms show – besides a polar bond to C (in CF_3), SEN(PC) = 1.0 is typical for slightly polar bonds – strong covalent bonding to neighbouring nitrogen atoms. The SEN(PN) = 1.4 is larger than expected for a polar σ bond and indicates appreciable π bond character providing additional bond stabilization. This reasoning is in line with the relatively short PN bond distances of ≈ 160 pm which one would associate with a double bond (single bond PN distance ≈ 168 pm [14], "triple bond" distance in PN 149 pm [15]): the (polar) σ bond is stabilized by Coulomb attractions (product of atomic charges of P and N is -0.6 to -0.8) and slight π bond contributions, vide infra.

A more detailed – although not always easy to interpret – picture is provided by the contour diagrams of high-lying MOs of **1** given in Fig. 2. All high-lying MOs arise from the (two) lone pairs of N atoms, which are divalent in N^-. Let us first consider the orbitals of π type: $28b_2, 29b_2, 21a_2$. The MO $28b_2$ is the most stable of these, it is dominantly localized on N4, the nitrogen atom opposed to V. There are, however, clearly visible delocalizations to the neighbouring P atoms. The P contributions to $28b_2$ appear to be dominantly of d type since the nodal surface cuts through the location of P (note that the contour lines correspond to a plane above the ring plane, which is a nodal plane of π MOs). This conclusion is confirmed by an inspection of the MO vector coefficients: the d(P) contribution is about 0.2 and the dominant p(P) coefficient about 0.1 for both basis sets considered. The MOs $21a_2$ and $29b_2$ are dominantly the $\pm$ combinations of π AOs of N2 and N3, Fig. 2. For MO $21a_2$ we find a clearly visible V $3d\pi$ contribution whereas delocalization into $3d\pi$ AOs of P is less pronounced for $21a_2$ and $29b_2$ than for $28b_2$. The π MOs thus show N $2p\pi \rightarrow$ P $3d\pi$ and N $2p\pi \rightarrow$ V $3d\pi$ backbonding effects. The picture emerging from the contour diagrams is supported by the MPA which give P gross charges $s^{5.1}p^{8.5}d^{0.6}$ (valence occupation $s^{1.1}p^{2.5}d^{0.6}$), i.e. a non-negligible d population.

The high-lying σ MOs $30b_1$ and $40a_1$ (not shown) are dominantly σ type lone pairs of N which are, however, more delocalized than the π MOs and are more difficult to interpret.

To conclude this section we return to the question of aromaticity, which in terms of molecular electronic structure is characterized by perfect delocalization of π MOs. In **1** we do not find this situation. The π type MOs do not delocalize in the sense of aromaticity. The π AOs on N2 and N3 are equivalent by symmetry and contribute to MOs in a $\pm$ combination (symmetry b_2 and a_2). The corresponding MOs $29b_2$ and $21a_2$ are virtually degenerated in energy, the orbital energies of 12.8 eV and 12.7 eV indicate a negligible interaction between the π AOs on N2 and N3 only. The contour diagrams of $29b_2$ furthermore does not show an appreciable interaction with the π AO on N4. The latter dominates the MO $28b_2$ which is energetically well separated, orbital energy 14.1 eV, from the other π type MOs. The energetic stability of $28b_2$ – dominantly on N4 – is by the way in accord with the less pronounced electronic charge of N4 ($q \approx -.75$) as compared to N2 and N3 ($q \approx -.95$). Our investigations thus do not reveal any significant interaction of nitrogen π AOs which would be characteristic of aromaticity.

5. Discussion and review

The structure determination of **1** within the SCF approximation presented in Sect. 3 agrees with results from X-ray diffraction within the typical error margins of both methods.

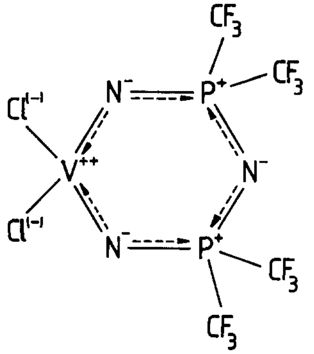

Fig. 3. Schematic representation of the electronic structure of the ring system in **1**. *Full lines* indicate (polar) σ bonds, *dashed arrows* π backbonding

The analysis of the electronic structure shows – as a reasonable zeroth-order approximation – divalent N^- and tetravalent P^+ atomic states. The nitrogen lone pair electrons are partly delocalized into low-lying orbitals of the neighbouring atoms P and V. As a result, one has (polar) σ bonds P–N and V–N, strongly stabilizing Coulomb interactions, and additional weak stabilizations through delocalization of nitrogen lone pairs into low-lying unoccupied AOs of neighbouring atoms. This state of affairs is depicted in Fig. 3. The structure constants are in line with this reasoning: the PN distance of 160 pm is much shorter than expected for a single bond (168 pm [14], the triple bond in gaseous PN has $r_e = 149$ pm [15]); the large (ring) angles of N (121° and 129°) are most easily rationalized for divalent N^-: the relatively small NVN angle (104°) points to strong d participation in the NV σ bonds, which favours smaller (than tetrahedral) angles.

The nitrogen lone pairs of π type (MOs $28b_2, 29b_2, 21a_1$) show only very weak interactions with each other. The MO $28b_2$ is localized on N4 (opposing V in the ring), the MOs $29b_2$ and $21a_2$ (which are the $\pm$ combination of π AOs on N2, N3) differ by only 0.1 eV in orbital energy which indicates very weak interaction of the π AOs.

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