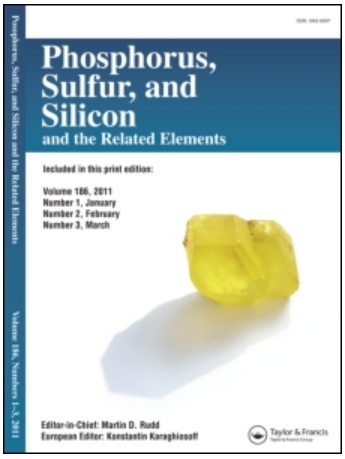

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Crystal Structure and Spectroscopic Investigation of 1,3-Dichloro-1,3-Diazetidine-2,4-Dione and 1,3 - Bis(Trimethylsilyl) -1,3- Diazetidine- 2,4-Dione

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CRYSTAL STRUCTURE AND SPECTROSCOPIC INVESTIGATION OF 1,3-DICHLORO-1,3-DIAZETIDINE-2,4-DIONE AND 1,3-BIS(TRIMETHYLSILYL)-1,3-DIAZETIDINE-2,4-DIONE

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Abstract Crystal structures of 1,3-dichloro-1,3-diazetidine-2,4-dione (**1**) and 1,3-bis(trimethylsilyl)-1,3-diazetidine-2,4-dione (**2**) have been determined by X-ray crystallography, and new infrared and Raman data of **1** have been recorded in the solid state, leading to revised and complete fundamental frequency assignments. Both compounds show a planar ring with a trans-configuration of the substituents X [X = -Cl, $-Si(CH_3)_3$]. The angles between the C-N-C plane and the exocyclic N-X bond are quite different: 32.5(1)° in **1** and 2.5(2)° and 0.8(2)° in **2**. These values are extremes referring to the known structural data of 1,3-diazetidine-2,4-diones. A normal coordinate analysis together with ab initio and semi-empirical calculations have been performed for **1** in order to support the vibrational assignments. The general valence force field confirms the revised frequency assignments. For discussion of the coupling phenomena in this molecule, the normal modes of vibration are plotted in terms of atomic displacements.

CRYSTAL STRUCTURE

Compounds **1** and **2** lie around inversion centers and have approximate C_{2h} symmetry of the $(XNCO)_2$ fragments (X=Cl, Si) in the solid state. Fig. 1 shows the bonding distances in **1** and in one molecule of **2**, where the crystal structure contains two half molecules in the asymmetric unit. In the difference electron density maps, representing the difference between the actual observed electron density and the superposition of spherically averaged free-atom densities allowed for anisotropic thermal vibration, for **1** (s. Fig. 2) and **2**, the residual peaks lie 0.18Å (average) outside the internuclear connecting lines, indicating the occurrence of bent C-N bonds in the diazetidine rings. The details of the structure determinations will be published elsewhere[1].

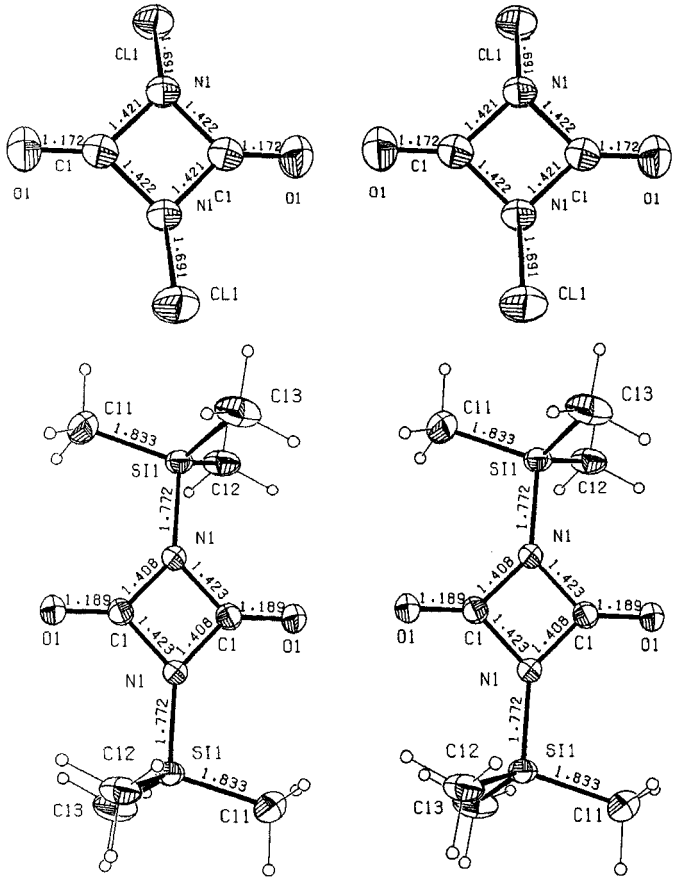

FIGURE 1. Stereographic projection of the molecules in the crystal structures of **1** (above) and **2** (below). The thermal ellipsoids are drawn at the 50% probability level, the hydrogen atoms are drawn with an arbitrary radius.[2a]

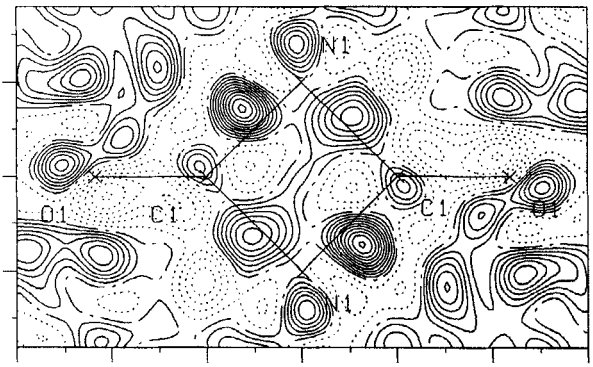

FIGURE 2. Difference electron density map in the ring plane of **1**. Contour lines are drawn with the interval ($0.02eÅ^{-3}$) of one standard deviation.[2b]

VIBRATIONAL ANALYSIS

The vibrational spectra of **1** have been investigated and interpreted on the basis of a C_{2v} molecular structure by Hester et al[5]. X-ray analysis as well as ab initio

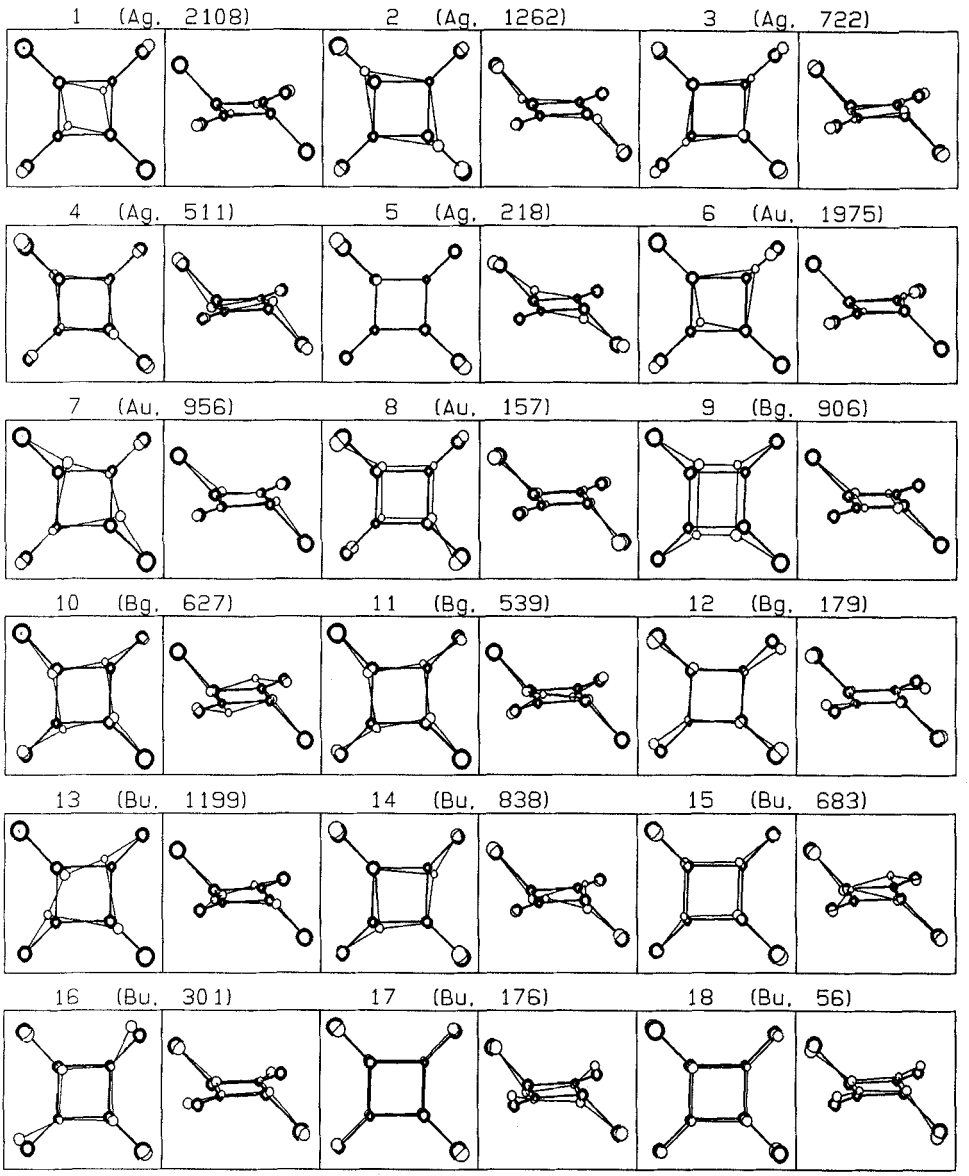

FIGURE 3. Atomic displacements during the fundamental vibrations of **1** as inferred from MNDO-PM3 data[3c]. [205]/27

ν	Mode	$\nu_a^{a)}$	$\nu_p^{b)}$	ν_{obs}	Int.	assignment[c)]
1	A_g	2033	2108	1933	m	0.8 CO str + 0.2 CN str
2	A_g	1241	1262	1197	m	0.5 CN str + 0.3 NCl str + 0.1 CO str
3	A_g	694	722	712	s	0.4 NCl str + 0.3 CN str + 0.1 NCl rock
4	A_g	455	511	459	vs	0.8 ring deformation + 0.1 NCl str
5	A_g	231	218	284	m	0.8 NCl rock + 0.1 NCl str
6	A_u	1931	1975	1819	vs	0.8 CO str + 0.2 CN str
7	A_u	1022	956	1004	s	0.8 CN str + 0.2 CO str
8	A_u	159	157	100	m	NCl wag
9	B_g	885	906	842	w	0.7 CN str + 0.3 CO wag
10	B_g	771	627	752	w	CO rock
11	B_g	675	539	648	w	0.6 CO wag + 0.3 CN str
12	B_g	180	179	196	m	0.9 NCl wag
13	B_u	1287	1199	1228	m	0.8 CN str + 0.1 NCl str
14	B_u	811	838	754	s	0.6 NCl str + 0.2 CO rock
15	B_u	740	683	705	m	0.7 CO rock + 0.2 NCl str
16	B_u	319	301	340	vw	0.9 CO wag + 0.1 CN str
17	B_u	166	176	208	m	0.8 pucker + 0.1 CO rock + 0.1 NCl rock
18	B_u	53	56	50	w	0.9 NCl rock + 0.1 pucker

TABLE 1. Calculated and Observed Frequencies (in cm^{-1}) of **1**.
[a)]Ab initio 3-21G*-frequencies × 0,89.[3] [b)]Semi-empirical MNDO-PM3 frequencies[4]. [c)]From potential energy distribution in full symmetry coordinates.

(3-21G*) and semi-empirical MNDO-PM3 geometries of **1** indicate that the ring adopts a planar conformation with an overall C_{2h} symmetry for the molecule. Thus the normal coordinates divide into $5A_g + 3A_u + 4B_g + 6B_u$ modes. We therefore began a program of remeasuring the vibrational spectra of **1**, and, aided by the ab initio and PM3 force field calculations, establishing conclusively its vibrational assignment (Table 1). The scaled ab initio spectrum reproduces most (89%) experimental frequencies to within 50 cm^{-1}. The diagram of the atomic displacements during the vibrations (Fig. 3) indicate the unique and significant occurrence of strong coupling leading to complicated modes. The force constant and PED (potential energy distribution) calculations within the GVFF was performed using the F-matrix program of Chacon & Matzke[6].

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