J. Am. Chem. Soc. 1980, 102, 5070-5073

Molecular, Electronic, and Crystal Structure of Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]selenadiazine

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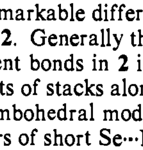
Abstract: Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]selenadiazine (**1**) crystallizes isomorphously with the homologous naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**2**) in the monoclinic space group $P2_1/a$. The lattice parameters of 1 are a = 15.099 (8) Å, b = 8.172 (5) Å, c = 3.863 (5) Å, β = 92.35 (2)°. Although the molecular structures of **1** and **2** are similar, there are some remarkable differences. The Se–N distance is 1.815 Å, indicating a smaller π-bond order than the chalcogen–nitrogen bond in **2**. Generally the bonds in the heterocyclic rings of 1 show more dominant single- or double-bond character than the equivalent bonds in **2** in accordance with reduced electron delocalization in **1**. In common with **2**, the crystal structure of **1** consists of stacks along which the molecular planes are separated by 3.42 Å, and are arranged in an analogous manner to the rhombohedral modification of graphite. As in **2**, coplanar molecules of 1 form ribbons in which they are connected by two pairs of short Se$\cdots$N contacts. These contact distances of 2.898 Å in **1** are even shorter than the similar S$\cdots$N contacts in **2** (3.104 Å). A linear correlation was found between the lengths of the intramolecular Se–N bonds and the intermolecular S$\cdots$N contacts for compounds with SeN_2– fragments, together with a corresponding relationship for compounds containing the SN_2– fragment.

Introduction

In the course of a systematic examination of sulfur–nitrogen compounds we previously reported on the X-ray structure analysis of naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**2**).[2a] The structure determination of the homologous naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]selenadiazine (**1**) is reported herein. The purpose of this determination was to study the effect on the electronic structure of the molecule brought about by replacing S with Se in the XN_2– units (X = S, Se). The chemical, physical, and spectroscopic properties of **1** are strikingly similar to those of **2** except for the ^{1}H NMR chemical shift value;[2b] the significantly smaller induced paramagnetic ring current in **1** is indicative of reduced electron delocalization in **1** as compared to **2**.[2b] In addition, we hoped to determine if the intermolecular interactions in the crystalline state of **1** were comparable to those found for **2**.



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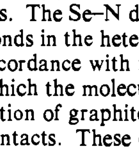

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Experimental Section

The title compound (1) crystallizes from 1,2-dichloroethane as long, metallic, greenish-brown, glistening plates. For the X-ray structure determination a crystal having the dimensions 0.17 × 0.10 × 1.10 mm^3 was used. On the basis of Weissenberg and precision photographs the monoclinic space group $P2_1/a$ was determined from the symmetry of the reflections and the systematic absences ($h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$). In order to determine the lattice parameters and reflection intensities we used a punch-tape controlled automatic single crystal diffractometer (Siemens AED). The lattice parameters are a = 15.099 (8) Å, b = 8.172 (5) Å, c = 3.863 (5) Å, β = 92.35 (2)°. From the volume of the unit cell (V = 476.3 Å^3), the molecular weight (M = 338.1), and measured density d_m = 2.34 g cm^{-3} (d_x = 2.357 g cm^{-3}) a unit cell content of two molecules (Z = 2) was calculated. The identity of the space groups and comparison of their lattice parameters (Table I) show that the homologous compounds **1** and **2** crystallize isomorphously. As in **2**, the crystallographic c axis is identical with the long-growth direction of the crystals. The crystal sizes of the compounds differ, such that in 1 crystal growth in the a direction is greater than in the b direction, while in **2** both directions exhibit similar crystal dimensions. Moreover, the marked tendency for twinning in the (100) plane of **2** was not found in 1. By the procedure of five-point measurement using $\theta/2\theta$ scan mode (Mo Kα radiation, θ_{max} = 25.67°) the intensities of 903 independent reflections were determined and LP corrections applied in the usual way. Of these, 199 were considered to be unobserved ($I < 2\sigma_I$, $|F_o| = 4\sigma_F$). On account of the large absorption ($\mu_{MoK\alpha}$ = 83.2 cm^{-1}) an absorption correction[3] of the reflection intensities was carried out.

Table I. Comparison of Crystallographic Parameters of 1 and 2

	1	2
a, Å	15.099	14.935
b, Å	8.172	8.304
c, Å	3.863	3.794
β, deg	92.35	91.53
V, Å	476.3	470.4
Z	2	2
d_x, d_m, g cm^{-3}	2.357, 2.34	1.725, 1.72

Structure Determination and Refinement

Since the molecules of 1 and 2 crystallize isomorphously, the least-squares refinement was started with the atomic coordinates of **2**. The structure has been refined first with isotropic and then, with the exception of H-atoms, anisotropic thermal parameters (full matrix, unit weights). The unobserved reflections were not included in the calculation of the parameter shifts when $|F_o| \geq |F_c|$. Moreover, in the last refinement cycles, 13 reflections with $\Delta F = ||F_o| - |F_c|| > 4$ were omitted. The absorption corrected data resulted in an R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.037. Utilizing the non-absorption-corrected data the significantly higher R value of 0.054 was obtained. Computations were carried out on an Amdahl 470 computer, using a modified version[4] of the X-RAY 67 program system.[5] The atomic scattering factors for C, N, and Se were taken from the International Tables for X-ray Crystallography,[6] and those for H were taken from Stewart, Davidson, and Simpson.[7] Table II contains

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(1) (a) Max-Planck-Institut für Biochemie, Abteilung für Strukturforschung I; (b) Bell Laboratories.

(2) (a) A. Gieren, V. Lamm, R. C. Haddon, and M. L. Kaplan, *J. Am. Chem. Soc.*, **101**, 7277 (1979); (b) R. C. Haddon, M. L. Kaplan, and J. H. Marshall, *ibid.*, **100**, 1235 (1978); M. L. Kaplan, R. C. Haddon, F. C. Schilling, J. H. Marshall, and F. B. Bramwell, *ibid.*, **101**, 3306 (1979).

(3) G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, **24**, 348 (1968).

(4) W. Hoppe, J. Gassmann, and K. Zechmeister in "Crystallographic Computing", Munksgaard, Copenhagen, 1970, p 26.

(5) J. M. Stewart, "The X-RAY 67 System", Technical Report TR-67-58, Computer Science Center, University of Maryland, College Park, Md., 1967.

(6) "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1 A.

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Table II. Fractional Coordinates and Thermal Parameters of All Atoms

	Coordinates[a]		
atom	*x*	*y*	*z*
Se	0.39424 (4)	0.86894 (8)	0.94165 (18)
N(1)	0.5088 (3)	0.8410 (7)	0.8353 (13)
N(2)	0.3421 (4)	0.6784 (7)	0.7987 (14)
C(1)	0.3858 (4)	0.5664 (8)	0.6506 (16)
C(2)	0.3356 (4)	0.4212 (9)	0.5486 (18)
C(3)	0.3717 (4)	0.2937 (9)	0.3905 (19)
C(4)	0.4659 (4)	0.2900 (8)	0.3171 (15)
C(5)	0.5196 (4)	0.4346 (7)	0.4194 (15)
H(1)	0.283 (5)	0.432 (9)	0.591 (18)
H(2)	0.344 (4)	0.210 (8)	0.322 (16)

			Thermal Parameters[b]			
atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se	1.91 (3)	2.00 (3)	2.46 (3)	0.27 (2)	0.25 (2)	−0.64 (2)
N(1)	1.8 (2)	2.1 (2)	1.8 (2)	−0.3 (2)	−0.1 (2)	−0.3 (2)
N(2)	1.9 (2)	2.1 (2)	2.4 (2)	−0.1 (2)	0.4 (2)	−0.6 (2)
C(1)	2.0 (3)	2.0 (3)	2.1 (3)	0.1 (2)	−0.1 (2)	0.1 (2)
C(2)	1.3 (2)	2.6 (3)	2.8 (3)	0.0 (2)	0.2 (2)	−0.1 (2)
C(3)	1.8 (3)	1.7 (3)	3.4 (3)	−0.6 (2)	0.2 (2)	−0.6 (2)
C(4)	2.1 (3)	2.6 (3)	1.2 (2)	−0.1 (2)	0.0 (2)	−0.2 (2)
C(5)	1.7 (2)	1.6 (2)	1.5 (2)	−0.1 (2)	−0.1 (2)	0.0 (2)
	b					
H(1)	2.4 (16)					
H(2)	1.1 (12)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and the following table. [b] The form of the anisotropic thermal ellipsoid is $\exp\{-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\}$.

Table III. Bond Distances and Angles[a]

	Bond Distances (Å)		
Se–N(2)	1.821 (5)	Se–N(1)	1.808 (5)
N(2)–C(1)	1.278 (9)	N(1)–C(4′)	1.287 (8)
C(1)–C(2)	1.454 (10)	C(3)–C(4)	1.463 (9)
C(1)–C(5′)	1.464 (9)	C(4)–C(5)	1.477 (9)
C(2)–H(1)	0.82 (8)	C(3)–H(2)	0.84 (7)
C(2)–C(3)	1.335 (10)		
C(5)–C(5′)	1.383 (9)		
	Bond Angles (deg)		
N(1)–Se–N(2)	103.2 (2)		
Se–N(2)–C(1)	121.5 (5)	Se–N(1)–C(4′)	120.9 (4)
N(2)–C(1)–C(2)	115.6 (6)	N(1)–C(4′)–C(3′)	114.5 (6)
N(2)–C(1)–C(5′)	127.8 (6)	N(1)–C(4′)–C(5′)	128.1 (6)
C(2)–C(1)–C(5′)	116.6 (6)	C(3)–C(4)–C(5)	117.3 (6)
C(1)–C(2)–C(3)	122.9 (6)	C(2)–C(3)–C(4)	121.6 (6)
C(4)–C(5)–C(5′)	119.9 (5)	C(1′)–C(5)–C(5′)	121.7 (5)
C(1)–C(2)–H(1)	111 (5)	C(4)–C(3)–H(2)	113 (4)
C(3)–C(2)–H(1)	126 (5)	C(2)–C(3)–H(2)	125 (4)

[a] The values within a line are equivalent by molecular symmetry.

the fractional coordinates and thermal parameters of all atoms. A list of the observed and calculated structure factors can be obtained from A. Gieren and V. Lamm.

Results and Discussion

The molecular structure of **1** is shown in Figure 1. The bond lengths and bond angles for **1** are summarized in Table III. The structure of **1** is analogous to that of **2**. As in **2**, the molecule is very nearly planar and possesses in addition to the crystallographic centrosymmetry the same higher *mmm* (D_{2h}) symmetry. In the crystal structure minor deviations from planar arrangement appear in the heterocyclic six-membered rings, showing a small tendency to a chair conformation. The greatest deviations from the ideal molecular plane are shown by the Se and N atoms (0.015 and 0.010 Å, respectively).

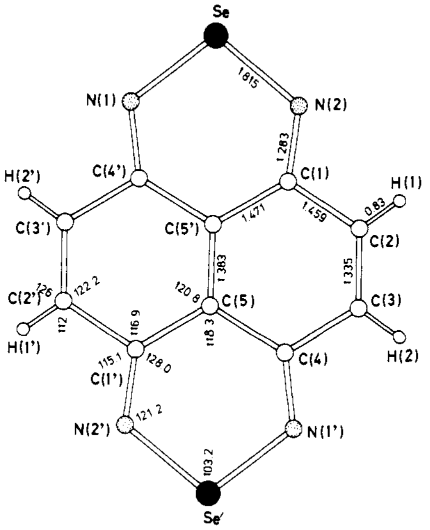

Figure 1. Molecular structure of naphthol[1,8-*cd*:4,5-*c′d′*]bis[1,2,6]selenadiazine (1). The given bond lengths and angles are mean values averaged over the molecular symmetry.

Table IV. Comparison of Bond Lengths and Bond Angles for 1 and 2 Averaged According to the Molecular *mmm* Symmetry (π-Bond Order in Parentheses)

	1(X = Se)	2(X = S)
	Bond Distances (Å)	
X–N(2)	1.815 (0.12)	1.649 (0.18)
N(2)–C(1)	1.283 (0.96)	1.314 (0.77)
C(1)–C(2)	1.459 (0.29)	1.454 (0.32)
C(1)–C(5′)	1.471 (0.23)	1.452 (0.33)
C(2)–C(3)	1.335 (0.95)	1.336 (0.95)
C(5)–C(5′)	1.383 (0.70)	1.380 (0.71)
C(2)–H(1)	0.83	0.96
	Bond Angles (deg)	
N(1)–X–N(2)	103.2	109.0
X–N–C(1)	121.2	121.4
N(2)–C(1)–C(2)	115.1	117.5
N(2)–C(1)–C(5′)	128.0	124.7
C(2)–C(1)–C(5′)	116.9	117.8
C(1)–C(2)–C(3)	122.2	121.6
C(1)–C(5′)–C(5)	120.8	120.6
C(1)–C(2)–H(1)	112	110
C(3)–C(2)–H(1)	126	128

The analogy between the molecular structures of **1** and **2** is in agreement with the strong similarities in their spectroscopic properties.[2] However, the ^{1}H NMR spectra provide evidence for a lower induced paramagnetic ring current in **1**.[2] This was explained in terms of a more localized structure for **1** as compared to **2**,[2] and this interpretation is supported by the results of the structure analysis.

Despite the similarities between the molecular structures of **1** and **2** some noticeable differences do appear in their bond lengths, bond orders, and bond angles. A comparison of corresponding quantities is given in Table IV. The principal and only significant differences between **1** and **2** occur in the heterocyclic six-membered rings. The Se–N bond distance of 1.815 Å corresponds to a low double-bond character in view of the Se–N single bond distance of 1.86 Å.[8] The bond order of the Se–N bond in **1** is considerably lower then the comparable S–N bond in **2**. Also different are the C–N bond lengths connecting the chalcogen–diimide systems with the naphthalene skeletons. In **1** these distances of 1.283 Å are significantly shorter than the 1.314 Å found in **2**. The reduction of the π-bond order of the X–N bond therefore results in an increase in the π-bond order of the neighboring C–N bond (Table IV). Moreover, the C–C bonds in the six-membered heterocyclic

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(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(8) H. Barnighausen, T. von Volkmann, and J. Jander, *Acta Crystallogr.*, **21** 571 (1966).

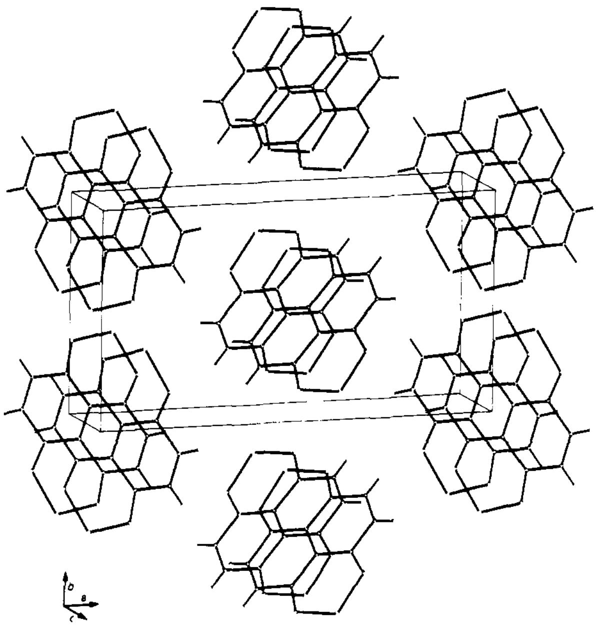

Figure 2. Crystal structure of naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]selenadiazine (1).

rings of **1** are about 0.02 Å longer than in **2**. In the heterocyclic rings of **1** it appears that the tendency toward pure single and double bonds is enhanced and their intermediate character is reduced in comparison to **2**. This result is equivalent to a reduced π-electron delocalization which is also evident in the ^{1}H NMR spectra.[2] The π-bond orders given in Table IV for S–N, C–N, and C–C bonds were calculated from the application of regression lines,[2a,9] to the measured bond lengths. The Se–N π-bond order was obtained by difference, using the assumption that the sums of the π-bond orders in **1** and **2** are equal.

A comparison of the homologous sulfur[10,11,13] structures with those of 3,4-diphenyl-1,2,5-selenadiazole[10] (**9**), 3,4-benzo-1,2,5-selenadiazole,[11] and anthra[1,2-*c*][1,2,5]selenadiazole-6,11-dione[12] (**14**) (the second and third pairs of Se and S compounds crystallize isomorphously) shows that by changing an SeN_2– unit to SN_2– the π-bond order of the chalcogen–nitrogen bond is increased, and that of the neighboring C–N bond is reduced. The difference between the π-bond orders of the chalcogen–nitrogen bonds of the homologous S and Se compounds is in accord with the idea that the facility for dπ-bond formation is reduced in going from the elements P, S, and Cl to their higher homologues.[14]

Crystal Packing

Based on the isomorphism of their crystal structures the molecular packings of **1** and **2** are very similar. As in **2** the molecules of **1** form stacks in the *c* direction with a layer sequence analogous to that of the rhombohedral modification of graphite (Figure 2). Moreover, short chalcogen–nitrogen contact distances lead to ribbon-like arrangements in the [011] and [01$\bar{1}$] directions in the same way as they are formed in **2**. The distance between the parallel molecular planes within the stacks is 3.42 Å. Because of the larger van der Waals radius of Se (2.0 Å)[15] the Se···Se contact distance within the stacks (identical with the lattice constant *c*) is lengthened by 0.07 Å to 3.863 Å in comparison with the analogous S···S contact distance in **2**. Increasing the distances of the molecular planes within the stacks by 0.02 Å causes the molecules of **1** to attain a slightly steeper slope, relative to the *c* axis. The angle formed by the normal to the molecular plane

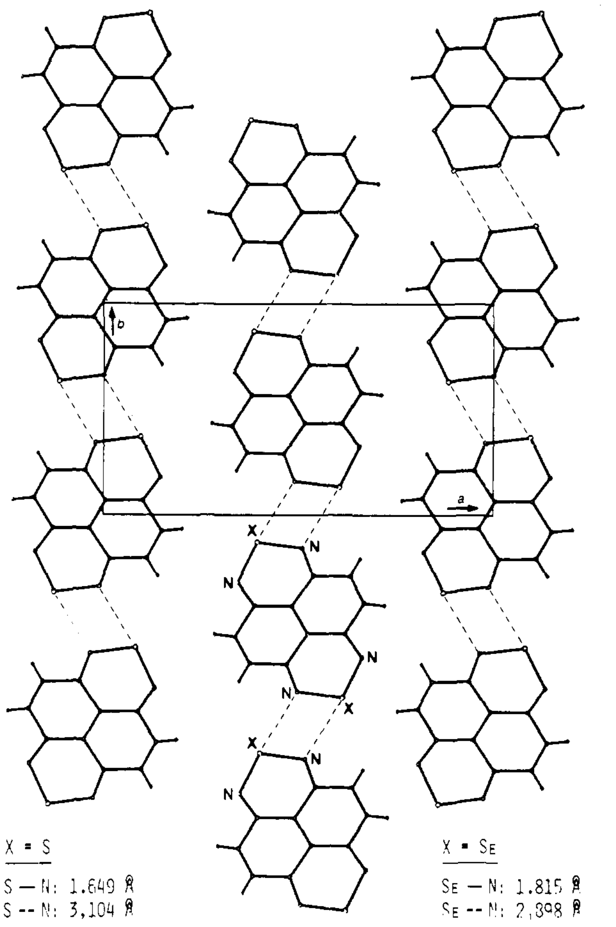

Figure 3. Ribbons in the crystal structure of **1**, showing the short Se···N contacts. For comparison the relevant parameters of the homologous sulfur compound **2** are given.

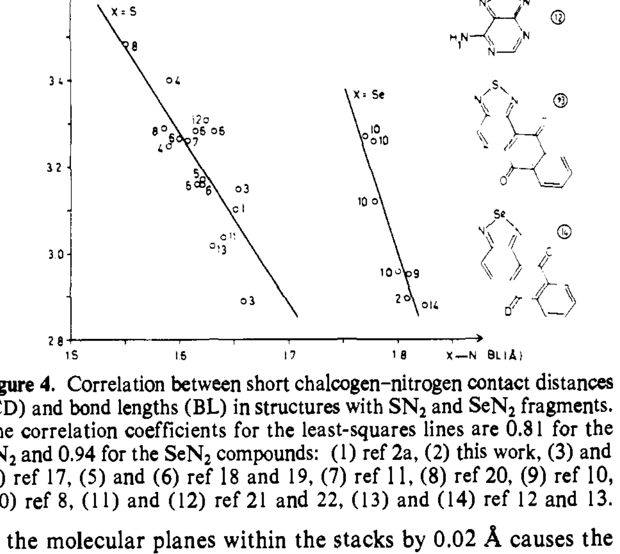

Figure 4. Correlation between short chalcogen–nitrogen contact distances (CD) and bond lengths (BL) in structures with SN_2 and SeN_2 fragments. The correlation coefficients for the least-squares lines are 0.81 for the SN_2 and 0.94 for the SeN_2 compounds: (1) ref 2a, (2) this work, (3) and (4) ref 17, (5) and (6) ref 18 and 19, (7) ref 11, (8) ref 20, (9) ref 10, (10) ref 8, (11) and (12) ref 21 and 22, (13) and (14) ref 12 and 13.

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(9) G. Häfelinger, *Chem. Ber.*, **103**, 2902 (1970).

(10) M. Mellini and S. Merlino, *Acta Crystallogr., Sect. B*, **32**, 1074 (1976).

(11) V. Luzzati, *Acta Crystallogr.*, **4**, 193 (1951).

(12) N. L. Klimasenko, L. A. Chetkina, and G. A. Gol'der, *Zh. Strukt. Khim.*, **14**, 515 (1973).

(13) N. L. Klimasenko, L. A. Chetkina, S. L. Ginzburg, M. G. Neigauz, and E. M. Smelyanskaya, *Zh. Strukt. Khim.*, **14**, 108 (1973).

(14) T. B. Brill, *J. Chem. Educ.*, **50**, 392 (1973).

(15) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 260, Table 7-20.

with the *c* axis is 26.2° in **2** while in **1** it is 27.7°. The S···S contact distance within the stacks of **2** is somewhat larger than the sum of the van der Waals radii, in contrast to the significantly shorter analogous Se···Se contact distance of 3.863 Å found in **1**. Because of the modified tilting toward the *c* axis the analogous graphite packing (rhombohedral modification)[16] in the stacks of **1** is somewhat more distorted than in **2**.

The most significant change relative to **2** occurs within the ribbons (Figure 3), in which the molecules are connected by way of the Se–N parallelograms. Although Se possesses a larger van der Waals radius than S, the Se···N contact distance of 2.898 Å (sum of van der Waals radii: S···N = 3.35; Se···N = 3.5 Å)[15] is even shorter than the S···N contact distance in **2**, 3.104 Å. This decrease is also manifested in the value of the smaller lattice constant in the *b* direction of **1** (Table I). Within the Se–N parallelograms the Se···Se contact distance is 3.857 Å and the N···N contact distances are 2.910 Å, which are both less than the sums of the van der Waals radii (4.0 and 3.0 Å, respectively). The Se···Se contact distances along the ribbons are similar to those within the stacks. As a result of the difference in orientation with respect to the *c* axis, the coplanarity of the molecules in the ribbon-like arrays is more easily achieved in **1** than in **2**. In **1** the molecular planes within the ribbons exhibit a deviation of only 0.02 Å from each other as compared to the value of 0.16 Å obtained for **2**.

The strong secondary valence or extravalent bonds within the ribbons are also demonstrated by the solution properties of **1** and **2**. For example, **1** is substantially less soluble than the already difficultly soluble **2**.[23] The fact that relative to **2** shorter intermolecular contact distances appear in **1** simultaneously with a reduction of the π-bond orders of the chalcogen–nitrogen bonds suggests a correlation between the chalcogen–nitrogen bond lengths and the contact distances in compounds containing SN_2– and SeN_2– units. At the time of publication of the structure determination of **2** we had proposed the existence of a correlation between S–N bond orders and contact distances in compounds containing the SN_2– grouping.[2a] In Figure 4 the chalcogen–nitrogen contact distances (≤ sum of the van der Waals radii + 0.2 Å) from crystal structures of compounds with SN_2– or SeN_2– units are plotted against the chalcogen–nitrogen bond distances. In both cases a linear relationship between contact and bond distances is found. From the slope of the straight lines it can be deduced that in compounds with SN_2– fragments the dependence of contact distance on bond distance is stronger than it is in structures having SeN_2– units.

Acknowledgments. A. Gieren and V. Lamm thank the Deutsche Forschungsgemeinschaft for support of this work. We thank H. D. Roth for helpful discussions.

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(16) W. N. Reynolds, "Physical Properties of Graphite", Elsevier, Amsterdam, 1968, p 3.

(17) M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran, and J. Kleppinger, *J. Am. Chem. Soc.*, **98**, 3844 (1976).

(18) S. Harkema, *Acta Crystallogr., Sect. B*, **34**, 2927 (1978).

(19) B. D. Sharma and J. Donahue, *Acta Crystallogr.*, **16**, 891 (1963).

(20) A. Gieren, Ch. Hahn, B. Dederer, H. W. Roesky, and N. Amin, *Z Anorg. Allg. Chem.*, **447**, 179 (1978).

(21) O. A. Mikhno, Z. I. Ezhkova, and G. S. Zhdanov, *Kristallografiya*, **18**, 99 (1973).

(22) E. Shefter, B. E. Evans, and E. C. Taylor, *J. Am. Chem. Soc.*, **93**, 7281 (1971).

(23) From comparison of the NMR proton line intensities of **1** and **2** in Me_2SO-d_6 at 100 °C. **1**, at the limit of its solubility (ca. 1 mg/mL), is less than one-tenth as soluble as **2**.

Structures of Some Bicyclic and Tricyclic Phosphoranes in Solution

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Abstract: A series of phosphoranes has been prepared from 5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octane (**4**) and 6-aza-2,10-dioxa-1-phosphabicyclo[4.4.0]decane (**9**). Two bicyclic derivatives, one from **4**, one from **9** (**11** and **13**), which have two methoxy groups bonded to phosphorus have favored structures in which the rings span from equatorial to apical positions. Compounds derived from **4** in which a five-membered ring containing two oxygens (**15** and **18**) or two sulfurs (**19**) bonded to phosphorus undergo intramolecular ligand reorganization at room temperature via a C_{2v} structure in which the five-membered ring spans two equatorial positions. At reduced temperatures the ligand reorganization is slowed on the NMR time scale. Condensation of biacetyl with **9** affords a phosphorane, **14**, which undergoes rapid ligand reorganization at room temperature. This process does not involve a five-membered ring which spans two equatorial positions.

A number of caged polycyclic phosphoranes have been synthesized and their structures have been studied by X-ray crystallography and NMR measurements.[1] The few compounds of this class that have been investigated by X-ray crystallography exist as trigonal bipyramids (TBP) or very nearly so in the solid state. An understanding of the structures of these molecules in solution has not been realized. A few observations have provided some limitations on the structural possibilities. For example, compounds containing a five-membered ring bonded to phoshorus which is at the bridgehead of a bicyclic ring system containing six-membered rings (a typical example is **1**) have NMR spectra that are only consistent with rapid intramolecular permutational isomerizations, "pseudorotations". These isomerizations have been found to be rapid over the entire range of temperatures investigated. Various mechanisms for the isomerizations have been discussed and low-energy structures have been suggested.[2,3] A number of similar compounds containing one or more five-membered rings in the bicyclic moiety have also been prepared, for

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(1) (a) W. S. Sheldrick, *Top. Curr. Chem.*, **73**, 1–49 (1978); (b) R. R. Holmes, *Acc. Chem. Res.*, **12**, 257 (1979).

(2) F. Ramirez and I. Ugi, *Bull. Soc. Chim. Fr.*, 453 (1974).

(3) R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).

0002-7863/80/1502-5073$01.00/0