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Contribution from the Department of Chemistry,
University of Windsor, Windsor, Ontario, N9B 3P4 Canada

ESCA Investigations of Group 4 Derivatives. 4. Binding Energies of Hydrido(methyl)germanes and -silanes and of Hydrido(halo)methylgermanes and -silanes

John E. Drake,* Chris Riddle, Boris Glavinčevski,
Krystyana Gorzelska, and H. Ernest Henderson

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We have reported[1,2] the core-level binding energies of all atoms in series of halo(methyl)germanes and -silanes of the type Me_nMX_{4-n}, where M = Ge or Si, X = F, Cl, Br, or I, and $n = 0$–4. In general, all of the observed binding energies increase in a stepwise fashion as methyl groups are replaced by halogen atoms, as expected if the latter have a greater electron-withdrawing capacity than the methyl groups. Thus, as the degree of substitution increases, so the central atoms (and any remaining carbon atoms) become relatively more positively charged and the binding energies (C 1s, Ge 3d, Si 2p) all increase. Further, as the "competition" from the other halogen atoms increases, so each halogen is relatively *less* negatively charged and so the binding energies (F 1s, Cl 2p, Br 3d, I 3d) also progressively increase. In conjunction with these studies, calculations were carried out which related the partial charges on atoms to the observed binding energies. The simple calculations were based on the electronegativity-equalization method of Huheey[3] with the added concept that the bonding orbitals of the halogen utilize varying degrees of s-orbital participation.[4] These EESOP (electronegativity equalization involving s-orbital participation) calculations "explain" the similar effective electronegativities of the halogens as arising from an increasing s-orbital participation along the series Cl < Br < I, which differs for germanium and silicon. (A similar concept has been employed in NQR studies[5] while other calculations have suggested 0 and 20% s character respectively for fluorine and chlorine.[6]) The implicit assumption that contributions from "relaxation energy" are at least consistent within these related compounds[7] seems to be supported, because the calculated partial charges correlate exceptionally well with the observed binding energies indicating that the changes in binding energies are reflecting changes in electronic distribution. With this background, we turn to a study of the hydrido(halo)methylgermanes and -silanes.

Experimental Section

Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer, using magnesium Kα X radiation (1253.6 eV) for photoelectron excitation. Samples were introduced in the vapor phase at pressures close to 5×10^{-5} Torr. Argon gas was bled in to form 20% of total sample. Binding energies were referenced to the argon $2p_{3/2}$ level at 248.63 eV (C 1s, F 1s, Cl $2p_{3/2}$, I $3d_{5/2}$) or to the neon 2s level at 48.47 eV (Ge 3d, Si 2p, Br $3d_{5/2}$).[4] Details of the data-accumulation procedures and the curve-fitting program are given in part 1.[1]

Table I. Core-Electron Binding Energies (BE) for the Hydrido(methyl)- and Hydrido(halo)methyl Derivatives of Germanium and Silicon

Compd	Binding energy,[a] eV					
			C 1s		X[b]	
	Ge 3d	Si 2p	Ge	Si	Ge	Si
Me_4M	36.11	106.02	289.82	289.78		
Me_3MH	36.35	106.18	289.88	289.90		
Me_2MH_2	36.68	106.71	290.04	290.14		
$MeMH_3$	36.98	106.95	290.26	290.31		
MH_4	37.32	107.31				
Me_2HMF[c]	37.74	107.63	290.30	290.33	690.81	692.25
MeH_2MF[c]	37.65	108.01	290.70	290.53	691.29	692.51
$MeHMF_2$	39.03	109.04	291.03	290.80	691.80	692.96
Me_2HMCl	37.52	107.38	290.38	290.24	205.26	205.68
MeH_2MCl	37.80	107.76	290.74	290.45	205.66	205.97
$MeHMCl_2$	38.47	108.54	290.89	290.68	205.81	206.23
Me_2HMBr	37.49	107.27	290.34	290.16	75.34	75.58
MeH_2MBr	37.83	107.70	290.52	290.55	75.48	75.86
$MeHMBr_2$	38.35	108.27	290.75	290.66	75.68	76.12
Me_2HMI	37.62	107.12	290.20	290.28	625.74	626.02
MeH_2MI	37.48	107.37	290.55	290.42	626.12	626.34
$MeHMI_2$	38.24	107.95	290.76	290.37	626.26	626.29

[a] Values corrected relative to Ar $2p_{3/2} = 248.63$ eV;[11] uncertainty ±0.5 eV, except that Ge 3d, Si 2p, and Br $3d_{5/2}$ are reported relative to Ne 2s at 48.47 eV.[11] [b] X corresponds to F 1s, Cl $2p_{3/2}$, Br $3d_{5/2}$, and I $3d_{5/2}$. [c] Partial overlap of F 2s peak with Ge 3d peak occurs resulting in a larger error in the assignment of the Ge 3d peak.

Materials. The hydrido(methyl)germanes and -silanes and the halo(hydrido)methylgermanes and -silanes were either obtained commercially (Laramie Chemical Co., Ventron Corp., Alfa Products, Matheson Gas Products, Petrarch Systems) or prepared by standard methods. In all cases, the materials were purified by vacuum techniques and identified by their ^1H NMR and vibrational spectra.

Charge Calculations. The previously described[1] mode of EESOP calculation is based on the relationship $\chi_M = a + b\delta_M$ relating the orbital electronegativity of an element, χ_M, to the partial charge δ_M, on that element.[3] As in our work on bromo- and iodo(methyl)germanes and -silanes, we obtain a and b values for the halogens for varying orders of s-orbital participation by interpolating between the limiting values.[2] The literature value of $\chi_H = 7.17 + 12.85\delta_H$[3] was used in the initial calculations to obtain the partial charges listed in part a of Tables II–VII,[8] along with the values of χ_M (M = Si, Ge, F, Cl, Br, I) shown in the tables which are in all cases identical with those values quoted earlier.[2] In subsequent calculations the value of $\chi_H = 8.7 + 12.85\delta_H$ was used to obtain the values for partial charge in part b of Tables II–VII.[8]

Results and Discussion

The experimentally observed core-level binding energies for the halo(hydrido)methylgermanes and -silanes, Me_2MHX, $MeMH_2X$, and $MeMHX_2$ (M = Ge, Si; X = F, Cl, Br, I), are given in Table I, along with those of the hydrido(methyl)germanes and -silanes, Me_nMH_{4-n} (M = Ge, Si; n = 0, 1, 2, 3). For the hydrido(methyl)germanes and -silanes it is clear that the observed binding energies increase in a stepwise fashion as the methyl groups are replaced by hydrogen atoms, in an analogous fashion to that observed with the halogens[1,2] but with lesser increments. The progression is as expected if hydrogen is acting as a "weakly electronegative" halogen but still with *more* electron-withdrawing power than the methyl group. Such a concept rationalizes, in qualitative terms, the general trends within all of the hydrido(halo)methylgermane and -silane series and is consistent with the fact that the polarity of the bonds has been shown to be Si(δ+)–H(δ−) in alkylsilanes.[9] Also, reactions of germanium

Table II. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) (eV) for the Germanium 3d Level in the Hydrido-Germane Series

	a^a					b^a		
Compd	δ_{Ge}	BE(calcd)	ΔBE	ΔBE/H	BE(exptl)	δ_{Ge}	BE(calcd)	ΔBE
Me_3GeH	−0.030	35.80	0.55	0.55	36.35	+0.009	36.40	−0.05
Me_2GeH_2	−0.050	35.50	1.18	0.59	36.68	+0.027	36.65	0.03
$MeGeH_3$	−0.070	35.20	1.78	0.59	36.98	+0.045	36.95	0.03
GeH_4	−0.090	34.90	2.42	0.61	37.32	+0.063	37.20	0.12
Me_2GeHF	+0.052	37.00	0.74	0.74	37.74	+0.092	37.65	0.09
$MeGeH_2F$	+0.030	36.65	1.00	0.50	37.65	+0.111	37.90	−0.25
$MeGeHF_2$	+0.140	38.40	0.63	0.63	39.03	+0.182	39.00	0.03
Me_2GeHCl	+0.042	36.90	0.62	0.62	37.52	+0.079	37.45	0.07
$MeGeH_2Cl$	+0.022	36.60	1.20	0.60	37.80	+0.096	37.70	0.10
$MeGeHCl_2$	+0.108	37.90	0.57	0.57	38.47	+0.145	38.45	0.02
Me_2GeHBr	+0.038	36.85	0.64	0.64	37.49	+0.074	37.40	0.09
$MeGeH_2Br$	+0.019	36.55	1.28	0.64	37.83	+0.091	37.60	0.23
$MeGeHBr_2$	+0.097	37.75	0.60	0.60	38.35	+0.130	38.20	0.15
Me_2GeHI	+0.027	36.70	0.92	0.92	37.62	+0.063	37.20	0.42
$MeGeH_2I$	+0.009	36.40	1.08	0.54	37.48	+0.079	37.45	0.03
$MeGeHI_2$	+0.075	37.40	0.84	0.84	38.24	+0.108	37.90	0.34

[a] Partial charges δ calculated by EESOP[1,2] assuming that germanium is using sp^3 hybrid orbitals, $\chi_{Ge} = 8.07 + 6.82\delta_{Ge}$; that the carbon atom is treated as an "unbonded tetrahedral carbon atom" using $\chi_C = 7.98 + 13.27\delta_C$; that there are 0, 11%, 16%, and 19% s character on fluorine, chlorine, bromine, and iodine, respectively, using $\chi_{Cl} = 10.47 + 11.11\delta_{Cl}$, $\chi_{Br} = 9.98 + 9.11\delta_{Br}$, and $\chi_I = 9.54 + 8.29\delta_I$; and that for hydrogen (a) $\chi_H = 7.17 + 12.85\delta_H$ and (b) $\chi_H = 8.7 + 12.85\delta_H$.

Table III. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) for the Carbon 1s Level in the Hydrido-Germane Series

	a^a				b^a		
Compd	δ_C	BE(calcd)	ΔBE	BE(exptl)	δ_{Ge}	BE(calcd)	ΔBE
Me_3GeH	−0.008	289.75	0.13	289.88	0.012	290.00	−0.12
Me_2GeH_2	−0.019	289.60	0.44	290.04	0.021	290.10	−0.06
$MeGeH_3$	−0.029	289.50	0.76	290.26	0.030	290.20	0.06
Me_2GeHF	−0.034	290.30	0.00	290.30	0.054	290.50	−0.20
$MeGeH_2F$	0.022	290.10	0.60	290.70	0.063	290.60	0.10
$MeGeHF_2$	0.079	290.80	0.23	291.03	0.100	291.10	−0.07
Me_2GeHCl	0.028	290.20	0.18	290.38	0.048	290.45	−0.07
$MeGeH_2Cl$	0.018	290.05	0.69	290.74	0.056	290.55	0.19
$MeGeHCl_2$	0.063	290.60	0.29	290.89	0.081	290.85	0.04
Me_2GeHBr	0.027	290.15	0.21	290.34	0.045	290.40	−0.06
$MeGeH_2Br$	0.017	290.05	0.47	290.52	0.053	290.50	0.02
$MeGeHBr_2$	0.057	290.55	0.20	290.75	0.074	290.75	0.00
Me_2GeHI	0.021	290.10	0.10	290.20	0.039	290.30	−0.10
$MeGeH_2I$	0.012	290.00	0.55	290.55	0.047	290.40	0.15
$MeGeHI_2$	0.046	290.40	0.36	290.76	0.062	290.60	0.16

[a] See footnote to Table I.

Table IV. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) for the Fluorine 1s, Chlorine $2p_{3/2}$, Bromine $3d_{5/2}$, and Iodine $3d_{5/2}$ Levels in the Hydrido-Germane Series

	a^a				b^a		
Compd	δ_X	BE(calcd)	ΔBE	BE(exptl)	δ_X	BE(calcd)	ΔBE
Me_2GeHF	−0.237	689.90	0.91	690.81	−0.201	690.70	0.11
$MeGeH_2F$	−0.225	690.20	1.09	691.29	−0.193	690.90	0.39
$MeGeHF_2$	−0.182	691.10	0.70	691.80	−0.165	691.70	0.10
Me_2GeHCl	−0.190	204.75	0.51	205.26	−0.167	205.10	0.16
$MeGeH_2Cl$	−0.202	204.60	1.06	205.66	−0.157	205.30	0.36
$MeGeHCl_2$	−0.150	205.35	0.46	205.81	−0.127	205.75	0.06
Me_2GeHBr	−0.182	74.90	0.44	75.34	−0.154	75.25	0.09
$MeGeH_2Br$	−0.196	74.70	0.78	75.48	−0.142	75.40	0.08
$MeGeHBr_2$	−0.137	75.50	0.18	75.68	−0.112	75.75	−0.07
Me_2GeHI	−0.155	625.55	0.19	625.74	−0.126	625.80	−0.06
$MeGeH_2I$	−0.170	625.40	0.72	626.12	−0.112	626.00	0.12
$MeGeHI_2$	−0.115	625.95	0.31	626.26	−0.089	626.00	0.26

[a] See footnote to Table II.

and silicon hydrides can usually be explained in terms of a nucleophilic attack of an electropositive center at germanium or silicon.[10]

We now return to the charge calculations to see if the correlations reported earlier[1,2] persist in the hydrido series. The plots of binding energies as a function of calculated partial charge based on our EESOP results on halo(methyl)germanes and -silanes (Figure 1)[8] are used as reference bases. The partial charges on all atoms in the hydrido series are calculated using the same values of χ_M as were used in preparing Figure 1, with the addition of a value for the electronegativity of hydrogen, $\chi_H = 7.17 + 12.85\delta_H$. Then the plots in Figure 1

Table V. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) for the Silicon 2p Level in the Hydrido–Silane Series

	a[a]					b[a]		
Compd	δ_{Si}	BE(calcd)	ΔBE	ΔBE/H	BE(exptl)	δ_{Si}	BE(calcd)	ΔBE
Me_3SiH	0.038	105.25	0.93	0.93	106.18	0.070	106.35	−0.17
Me_2SiH_2	0.022	104.80	1.91	0.96	106.71	0.085	106.75	−0.04
$MeSiH_3$	0.006	104.25	2.70	0.90	106.95	0.100	107.10	−0.15
SiH_4	−0.011	103.85	3.46	0.87	107.31	0.114	107.45	−0.14
Me_2SiHF	0.104	107.20	0.43	0.43	107.63	0.137	108.05	−0.42
$MeSiH_2F$	0.086	106.75	1.26	0.63	108.01	0.152	108.45	−0.44
$MeSiHF_2$	0.176	109.00	0.04	0.04	109.04	0.211	109.90	−0.86
Me_2SiHCl	0.083	106.70	0.68	0.68	107.38	0.114	107.45	−0.07
$MeSiH_2Cl$	0.067	106.30	1.46	0.73	107.76	0.128	107.85	−0.09
$MeSiHCl_2$	0.125	107.75	0.79	0.79	108.54	0.155	108.50	0.04
Me_2SiHBr	0.082	106.70	0.57	0.57	107.27	0.111	107.40	−0.13
$MeSiH_2Br$	0.066	106.30	1.40	0.70	107.70	0.125	107.75	−0.05
$MeSiHBr_2$	0.119	107.60	0.67	0.67	108.27	0.146	108.30	−0.03
Me_2SiHI	0.078	106.60	0.52	0.52	107.12	0.107	107.30	−0.18
$MeSiH_2I$	0.063	106.20	1.17	0.59	107.37	0.117	107.60	−0.23
$MeSiHI_2$	0.110	107.40	0.55	0.55	107.95	0.136	108.02	−0.07

[a] Partial charges δ calculated by EESOP[1,2] assuming that silicon is using sp^3 hybrid orbitals, $\chi_{Si} = 7.30 + 9.04\delta_{Si}$; that the carbon atom is treated as an "unbonded tetrahedral carbon atom" using $\chi_C = 7.98 + 13.27\delta_C$; that there are 0%, 5%, 11%, and 15% s character on fluorine, chlorine, bromine, and iodine, respectively, using $\chi_F = 12.18 + 17.36\delta_F$, $\chi_{Cl} = 9.87 + 11.22\delta_{Cl}$, $\chi_{Br} = 9.49 + 9.2\delta_{Br}$, and $\chi_I = 9.24 + 8.47\delta_I$; and that for hydrogen (a) $\chi_H = 7.17 + 12.85\delta_H$ and (b) $\chi_H = 8.7 + 12.85\delta_H$.

Table VI. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) for the Carbon 1s Level in the Hydrido–Silane Series

	a[a]				b[a]		
Compd	δ_C	BE(calcd)	ΔBE	BE(exptl)	δ_C	BE(calcd)	ΔBE
Me_3SiH	−0.025	289.50	0.40	289.90	−0.003	289.80	0.10
Me_2SiH_2	−0.036	289.40	0.74	290.14	0.007	289.95	0.19
$MeSiH_3$	−0.047	289.30	1.01	290.31	0.017	290.05	0.26
Me_2SiHF	−0.019	289.60	0.73	290.33	0.042	290.35	−0.02
$MeSiH_2F$	0.008	289.95	0.58	290.53	0.053	290.50	0.03
$MeSiHF_2$	0.069	290.70	0.10	290.80	0.092	291.00	−0.20
Me_2SiHCl	0.005	289.90	0.34	290.24	0.026	290.20	0.04
$MeSiH_2Cl$	−0.006	289.80	0.65	290.45	0.036	290.30	0.15
$MeSiHCl_2$	0.034	290.30	0.38	290.68	0.054	290.50	0.18
Me_2SiHBr	0.004	289.90	0.26	290.16	0.024	290.15	0.01
$MeSiH_2Br$	−0.006	289.80	0.75	290.55	0.034	290.30	0.25
$MeSiHBr_2$	0.030	290.20	0.46	290.66	0.048	290.45	0.21
Me_2SiHI	0.002	289.85	0.43	290.28	0.021	290.10	0.18
$MeSiH_2I$	−0.009	289.70	0.72	290.42	0.030	290.20	0.22
$MeSiHI_2$	0.024	290.15	0.22	290.37	0.042	290.35	0.02

[a] See footnote to Table V.

Table VII. Comparison of Calculated and Experimental Core-Electron Binding Energies (BE) for the Fluorine 1s, Chlorine $2p_{3/2}$, Bromine $3d_{5/2}$, and Iodine $3d_{5/2}$ Levels in the Hydrido–Silane Series

	a[a]				b[a]		
Compd	δ_X	BE(calcd)	ΔBE	BE(exptl)	δ_X	BE(calcd)	ΔBE
Me_2SiHF	−0.226	690.20	2.05	692.25	−0.209	690.50	1.75
$MeSiH_2F$	−0.236	689.90	2.61	692.51	−0.202	690.75	1.76
$MeSiHF_2$	−0.189	690.90	2.06	692.96	−0.171	691.35	1.61
Me_2SiHCl	−0.162	205.20	0.48	205.68	−0.137	205.60	0.08
$MeSiH_2Cl$	−0.175	205.00	0.97	205.97	−0.126	205.75	0.22
$MeSiHCl_2$	−0.128	205.70	0.53	206.23	−0.104	206.10	0.13
Me_2SiHBr	−0.158	75.20	0.38	75.58	−0.129	75.55	0.03
$MeSiH_2Br$	−0.173	75.00	0.86	75.86	−0.115	75.70	0.16
$MeSiHBr_2$	−0.121	75.65	0.47	76.12	−0.094	75.95	0.17
Me_2SiHI	−0.146	625.65	0.37	626.02	−0.115	625.90	0.12
$MeSiH_2I$	−0.162	625.50	0.84	626.34	−0.102	626.05	0.29
$MeSiHI_2$	−0.111	626.00	0.29	626.29	−0.083	626.25	0.04

[a] See footnote to Table V.

are used to read off a calculated binding energy corresponding to a particular charge. The partial charges and calculated binding energies are recorded in part a of Tables II–VII.[8]

It is immediately obvious that the calculated binding energies are lower than the experimental values. This is an inevitable consequence in any charge-equalization calculation.[11] Because $a = 7.17$ for χ_H and 7.98 (tetrahedral) or 7.45 (methyl group) for χ_C, any calculation will require that the hydrogen atom be relatively *less* electron withdrawing than the methyl group with the result that a *decrease* in the binding energy, rather than the observed *increase*, is predicted when hydrogen replaces a methyl group in these compounds.

Possibly, the experimental binding energies are increasing not as a consequence of an electronic distribution in the ground state but because of some other phenomenon—possibly relaxation, which may well be expected to predominate in the hydrides.[7,12] However, *all* charge calculations will predict the polarity of the Ge–H and Si–H bonds to be M($\delta-$)–H($\delta+$), contrary to dipole moment measurements[9] on alkylsilanes. Alternatively, we could assume that the binding energies are indeed changing as a reflection of electronic redistributions and reevaluate our charge calculations. To maintain the validity of our base plots (Figure 1) we cannot alter any χ values except that of χ_H. We therefore recalculate binding energies using the value $\chi_H = 8.7 + 12.85\delta_H$ (the value of *a* = 8.7 gives a good fit for GeH_4 and SiH_4 and fits the concept of a "weakly electronegative" halogen). The resulting comparisons between calculated and observed binding energies are given in part b of Tables II–VII. Allowing for the simplicity of the model, the total neglect of relaxation effects, and the arbitrary value of *a*, the agreement between calculated and experimental binding energies for *all* levels is remarkably good. As in our earlier paper,[1] the largest discrepancy is in the values of the Si 2p levels in the fluorosilanes. Thus, the EESOP calculations, which are ignoring pπ–dπ bonding, estimate too high a positive partial charge on silicon and too high a negative charge on fluorine resulting in an estimated binding energy that is considerably higher than experimental for silicon (Table V, part b) and lower for fluorine (Table VII, part b). Of course, pπ–dπ bonding, if present, would have the effect of reducing the positive charge on silicon and correspondingly decreasing the negative charge on fluorine. The same discrepancy is not seen for the Ge 3d levels in the fluorogermanes.

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Registry No. Me_4Ge, 865-52-1; Me_3GeH, 1449-63-4; Me_2GeH_2, 1449-64-5; $MeGeH_3$, 1449-65-6; GeH_4, 7782-65-2; Me_2HGeF, 34117-35-6; MeH_2GeF, 30123-02-5; $MeHGeF_2$, 30123-03-6; Me_2HGeCl, 21961-73-9; MeH_2GeCl, 29914-10-1; Me_4Si, 75-76-3; Me_3SiH, 993-07-7; Me_2SiH_2, 1111-74-6; $MeSiH_3$, 992-94-9; SiH_4, 7803-62-5; Me_2HSiF, 865-46-3; MeH_2SiF, 753-44-6; $MeHSiF_2$, 420-34-8; Me_2HSiCl, 1066-35-9; MeH_2SiCl, 993-00-0; $MeGeHCl_2$, 1111-82-6; Me_2GeHBr, 53445-65-1; $MeGeH_2Br$, 30123-09-2; $MeGeHBr_2$, 30123-10-5; Me_2GeHI, 33129-32-7; $MeGeH_2I$, 30123-01-4; $MeGeHI_2$, 30123-05-8; $MeSiHCl_2$, 75-54-7; Me_2SiHBr, 2441-22-7; $MeSiH_2Br$, 1631-88-5; $MeSiHBr_2$, 2441-24-9; Me_2SiHI, 2441-21-6; $MeSiH_2I$, 18089-64-0; $MeSiHI_2$, 16642-68-5.

Supplementary Material Available: Figure 1 showing core-level binding energies for the halo(methyl)germanes and -silanes as a function of δ (1 page). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
State University of New York at Buffalo, Buffalo, New York
14214

Crystal Structure of Tetrasulfur Tetranitride (S_4N_4) at 120 K

M. L. DeLucia and P. Coppens*

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Tetrasulfur tetranitride (S_4N_4) is the starting material for the synthesis of $(SN)_x$, the first superconducting polymeric material. It is an unusual cage compound (Figure 1), the room-temperature structure of which was established by Clark[1] and Sharma and Donohue.[2] The molecule in the crystal conforms closely to D_{2d} symmetry and may be considered as an eight-membered ring, folded back on itself so as to form two "across-the-ring" S–S distances of 2.576 (8) and 2.586 (8) Å at room temperature.[2] Though these distances are more than 1 Å shorter than the sum of the van der Waals radii, they are still considerably longer than a single S–S bond, which was listed by Hordvik as 2.10 Å,[3] or the S–S bond in *cyclo*-octasulfur which is 2.057 (1) Å.[4] The nature of the bonding in S_4N_4 has therefore been the subject of several publications. Bonding schemes by Mingos[5] and Gleiter[6] assign bonding character to the S–S interaction, while Banister[7] invokes d orbitals in a bonding scheme that also involves bonding between S atoms separated by two S–N bonds, such as S(1) and S(2). Theoretical calculations by the CNDO/BW,[8] SCF Xα,[9] and EHMO[10] methods also predict bonding mainly of p character in the "across-the-ring" S---S interaction.

The low-temperature crystallographic study was undertaken (a) to provide more accurate bond lengths, (b) to measure the temperature dependence of the S---S distances which should be small if the bond is of significant strength, (c) to obtain net atomic charges through a valence-shell population refinement, and (d) to obtain the detailed three-dimensional electron distribution for a more detailed analysis of the electronic structure of this compound.

We report here on the results of (a) and (b) and give a preliminary description of the charge density distribution. The detailed electron distribution and its comparison with results from theoretical calculations near the Hartree-Fock level by Rys and King will be discussed in a later publication.

Experimental Section

Tetrasulfur tetranitride was prepared as described by Jolly.[11] Crystals formed upon slow evaporation of a chloroform solution. X-ray data were collected at 120 K on an automated Picker diffractometer controlled by the Vanderbilt operating system.[12] Cooling was achieved with the self-regulating CT-38 cryostat.[13] Cell dimensions obtained by least-squares refinement of the orientation of 24 reflections are compared with neutron values[14] and room-temperature cell dimensions in Table I, which also lists other experimental information. A total

Table I. Physical and Crystallographic Data

molecular mass: 184.284 daltons
space group: $P2_1/n$
temp of data collection: 120 K
technique: θ–2θ step scan
wavelength: Mo Kα 0.7107 Å
$\rho_{\text{X-ray}}$: 2.297 g/cm^3

cell dimension	X-ray 120 K	neutron 125 K[a]	X-ray room temp[b]
a, Å	8.752 (2)	8.729	8.75
b, Å	7.084 (7)	7.100	7.16
c, Å	8.629 (2)	8.640	8.65
β, deg	93.68 (5)	93.20	92.5
Z	4	4	4

[a] Reference 14. [b] Reference 2.