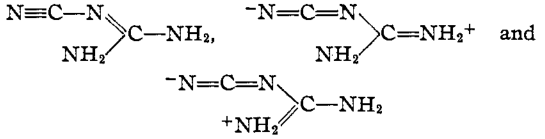
The author is indebted to Mr. P. A. Shaffer, Jr., who grew and mounted most of the crystals and assisted with the preparation and indexing of some of the photographs. Thanks are also due to Professor Pauling for encouragement and advice.

Summary

The crystal structure of dicyandiamide has been investigated. The monoclinic unit cell has $a = 15.00$ Å., $b = 4.44$ Å., $c = 13.12$ Å. and $\beta = 115° 20'$. The space group is $C2/c$ and there are eight molecules of $C_2N_4H_4$ per cell. The positions of the atoms have been found and correspond to a molecule which is a resonance hybrid, chiefly between structures



The packing of the molecules was found to be dominated by hydrogen bonds, one of which is of the rare bifurcated type. The properties of the compound have been discussed briefly in relation to the structure.

PASADENA, CALIF. RECEIVED MARCH 5, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 768]

An Electron Diffraction Investigation of the Molecular Structure of Tellurium Tetrachloride

BY D. P. STEVENSON AND VERNER SCHOMAKER

Introduction

It has been remarked by Pauling[1] that it is not known whether or not the unshared electron pair in molecules and complexes such as $SeCl_4$, TeC_4l, and $[AsCl_4]^-$ is stereochemically inert as it is in the compounds M_2SeBr_6, or stereochemically active as in ammonia-like compounds. From a discussion of the properties of the solid and dielectric constant measurements on dilute benzene solutions, Smyth, Grossman and Ginsburg[2] conclude that $TeCl_4$ has a large dipole moment. But this conclusion is insufficient to fix the structure of the molecule or to determine the steric effect of the unshared electron pair. Through the kindness of Professor J. H. Hildebrand, a pure sample of $TeCl_4$ which had been used for heat capacity determinations[3] was made available to us for the study of the structure of the molecule in the gas phase. The results of our study are reported in this paper.

Experimental

The apparatus used in this investigation has been described by Brockway.[4] The wave length of the electrons determined in the usual manner from transmission photographs of gold foil ($a_0 =$ 4.070 Å.) was 0.0618 Å. The photographs were taken with a camera distance of 10.86 cm.

The low volatility of the compound (b. p. 390°) necessitated the use of the high-temperature nozzle[5] in order to obtain sufficient gas pressure. The photographs were taken with the sample in the boiler at 250–350°. We believe that the material actually present in the diffracting jet of gas was monomolecular tellurium tetrachloride. Simons[6] has shown that tellurium tetrachloride vapor is not appreciably dissociated (into tellurium dichloride and chlorine) up to 500° and that below this temperature the vapor is unassociated. There is the possibility that some of the tellurium tetrachloride reacted with the various metallic parts of the boiler. The only probable volatile product of such reactions is tellurium dichloride. Moderate amounts of tellurium dichloride would have little effect on our determination inasmuch as the tellurium–chlorine distance[7] (2.36 ± 0.03 Å.) in tellurium dichloride is nearly the same as the value found here for tellurium tetrachloride, while the chlorine–chlorine scattering is small compared to the chlorine–chlorine scattering of tellurium tetrachloride.

The photographs show seven rings, two of which are asymmetric. Curve D of Fig. 1, to be dis-

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[1] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 172.

[2] C. P. Smyth, A. J. Grossman and S. A. Ginsburg, THIS JOURNAL, **62**, 192 (1940).

[3] K. J. Frederick and J. H. Hildebrand, *ibid.*, **60**, 2522 (1938).

[4] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[5] L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

[6] J. H. Simons, *ibid.*, **52**, 3488 (1930).

[7] W. Grether, *Ann. Physik*, **26**, 1 (1936).

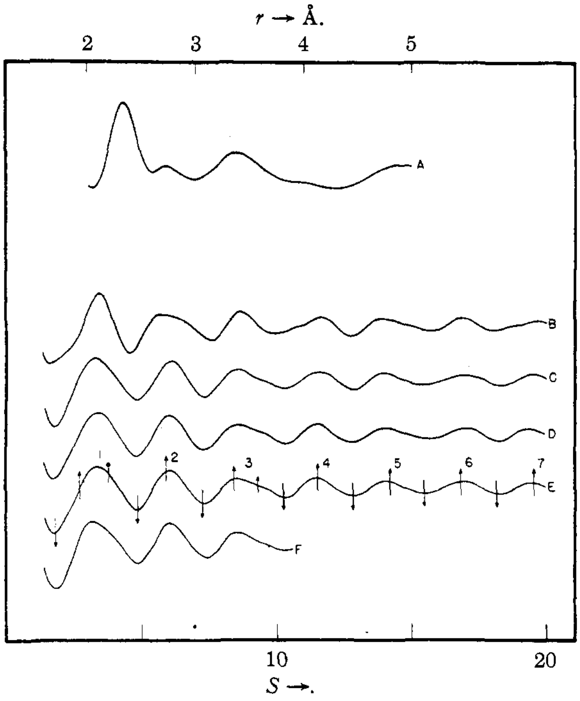

Fig. 1.—Curve A. Radial distribution function. Curve B. Regular tetrahedron, Te–Cl = 2.33 Å. Curve C. Trigonal bipyramid, Te–Cl = 2.33 Å., angles 90° and 120°. Curve D. Distorted trigonal bipyramid, Te–Cl = 2.33 Å., angles 93° and 120°. Curve E. Like D, but with temperature factor, a = 0.003, in coefficient of Cl–Cl terms. Curve F. Coplanar square. Te–Cl = 2.33 Å. Indistinguishable from curve E for S ⩾ 10.

cussed below, gives a good representation of the appearance of the photographs. The observed values of $s\left(s = \frac{4\pi}{\lambda}\sin\frac{\Theta}{2}\right)$ for the maxima and minima as well as the visually estimated relative intensities, I, are given in Table I.

TABLE I

Max.	Min.	I_0	C_n	s_0	s_c[a]	s_c/s_0
	1	−10	− 4	1.80	1.72	(0.956)[b]
1		8	4	2.71	3.34	(1.232)[b]
	1a	− 2	− 1	3.19	...	...
1a		6	4	3.77	...	...
	2	−10	− 8	4.84	4.84	1.000
2		10	10	5.91	6.04	1.022
	3	− 7	− 7	7.23	7.30	1.010
3		7	8	8.40	8.50	1.012
	3a	− 2	− 2	8.79	...	...
3b		4	4	9.27	...	...
	4	− 7	− 8	10.21	10.30	1.009
4		10	11	11.50	11.45	0.996
	5	−10	−10	12.80	12.70	0.992
5		10	9	14.20	14.10	0.993
	6	−10	− 8	15.44	15.50	1.004
6		10	7	16.83	16.90	1.004
	7	−10	− 5	18.13	18.20	1.004
7		10	4	19.53	19.40	0.993
				Average	1.003±0.007	

[a] From curve E. [b] Omitted because of unreliability of measurement.

Interpretation.—The radial distribution function[8] was calculated using the formula

$$D(l) = \sum_n C_n \frac{\sin ls_n}{ls_n} \qquad (1)$$
$$C_n = f(I_n, s_n)$$

The values of C_n were calculated in accordance with the recommendations of Schomaker[9] and are given in column 4 of Table I. The plot of $D(l)$ *vs.* l is given in Fig. 1, curve A. The strong peaks at 2.33 and 3.37 Å. undoubtedly correspond to interatomic distances in the molecule. The rather pronounced shoulder at 2.75 Å. is probably spurious, since the value 2.75 Å. does not correspond to an interatomic distance in any reasonable molecular model for tellurium tetrachloride. The 2.33 Å. peak corresponds to the Te–Cl distance (covalent radius sum, 2.36 Å.), while the other maximum at 3.37 Å. corresponds to a Cl–Cl distance. This interpretation leads to a bond angle of slightly more than 90° ($2.33\sqrt{2} = 3.30$). It is to be emphasized that there is only one maximum corresponding to a Cl–Cl distance. Several molecular models can now be eliminated from consideration. The molecule cannot have a regular tetrahedral structure, since for such a structure the Cl–Cl distance would be $2.33 \times \sqrt{8/3} = 3.82$ Å., while the radial distribution function gives 3.37 Å. for this distance. Models that can be derived by distortion of the regular tetrahedron with retention of the symmetry elements of the group C_{3v} would also be unsatisfactory. For example, a model with equal Te–Cl distances would have two equally important Cl–Cl distances, one greater than and the other less than 3.82 Å., in disagreement with the radial distribution function. A model having all equal Cl–Cl distances, three Te–Cl distances at the radial distribution function value, and one very much shorter Te–Cl distance (at about 1.7 Å.) would agree satisfactorily with the radial distribution function, but would be extremely improbable for structural reasons.

The radial distribution curve is compatible with models having equal or nearly equal Te–Cl distances, about four bond angles at 93°, and no more than one or two bond angles at any other value. Models satisfying these conditions can be

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[8] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[9] Verner Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.

derived by unsymmetrical distortion of a regular tetrahedron retaining the symmetry elements of D_{2d} or C_{2v}. A very flat tetrahedron D_{2d} or C_{2v} (limiting case: the coplanar square) is such a model. A slightly distorted trigonal bipyramidal model (C_{2v}) in which the unshared electron pair occupies one of the equatorial positions is another. In these models the two Cl–Cl distances at values other than 3.37 Å. contribute little to the scattering, especially if different from each other, and might be expected not to appear on the radial distribution curve.

Theoretical curves were calculated for a variety of molecular models based on the interpretation of the radial distribution function given above, and are shown in Fig. 1, curves B-F. Average values of $Z_i - f_i$ were used in place of the more commonly used Z_i in the scattering formula

$$I(s) = \sum Z_i Z_j \frac{\sin l_{ij}s}{l_{ij}s} \qquad (2)$$

because of the great disparity in the functions $(Z - f)/Z$ for tellurium and chlorine. The effect of the variation of $(Z - f)_{\mathrm{Cl}}/(Z - f)_{\mathrm{Te}}$ with s was found to be negligible. The various symbols in equation (2) have their usual significance.[2] The values of f were obtained from the tables of Pauling and Sherman.[10] The intensity curves for the various models, except curve B, were all found to be satisfactory with regard to the qualitative features of the photographs, although none of the curves reproduces the unusually sharp appearance of the inner edge of the first maximum. Although we are unable to advance a satisfactory explanation of this discrepancy, we are quite sure that it is not due to our not having found the correct model for the structure of the molecule. Some of the curves were found to give more satisfactory quantitative agreement than others. Thus it was found that the models which had four of the bond angles equal to 93° gave curves for which the quantitative agreement was much better than those for which the angles were 90°. It was further found impossible to distinguish between models with two pairs of Te–Cl distances (2.27 and 2.40 Å.) from the corresponding models with all four Te–Cl distances equal to 2.33 Å., or between the flattened tetrahedral and the trigonal bipyramidal models of symmetry C_{2v}. The best quantitative agreement was attained when a temperature factor (a = 0.003) was introduced into the coefficients of the Cl–Cl terms as is suggested by the greater width of the Cl–Cl peak of the radial distribution function. The quantitative comparison with the most satisfactory curve (curve E, Fig. 1) is given in Table I.

The results of our electron diffraction study of $TeCl_4$ may be summarized as follows. The average Te–Cl distance is 2.33 ± 0.02 Å. The only important Cl–Cl distance is 3.37 ± 0.06 Å., corresponding to a bond angle of 93 ± 3°. The molecule cannot have a structure with symmetry C_{3v}. It may have any of a number of structures with symmetry D_{2d}, C_{2v}, or lower symmetry. The coplanar square structure seems unlikely because in it the important bond angles are at 90°. The value of a used in the effective temperature factor is comparable to the values found for other similar molecules investigated at high temperatures.

Discussion.—Among the possible configurations for $TeCl_4$ discussed above as being compatible with the electron diffraction photographs, only those of the "trigonal bipyramidal" type would be expected to lead to the large dipole moment (2.5 D)[2] found by Smyth, Grossman and Ginsburg. We accordingly believe that $TeCl_4$ molecules have a configuration derived from the trigonal bipyramid, one of the equatorial positions being occupied by the unshared electron pair. According to our electron diffraction investigation, the equatorial–axial bond angles are about 93°; the equatorial bond angle is probably considerably less than 120° but greater than 90°, as is suggested by the arguments given below; and the axial–axial bond angle is accordingly about 170°.

Our first argument regarding the equatorial bond angle is based on Pauling's theory of directed valence[1] and the assumption that the structure is based on the trigonal bipyramid with no significant distortion of the axial straight angle. If the four bond orbitals and the orbital occupied by the unshared pair are formed from the configuration sp^3d_z, as seems likely because of the greater stability of s and p, the equatorial bond angle will be 120° provided that p_x and p_y are distributed equally among the equatorial bonds and the unshared pair. It seems likely that the unshared pair orbital will have more than $^1/_3$ (s,d_z) character and less than $^2/_3$ p character because of the greater coulombic stability of s, and in spite of the lesser coulombic stability of d. This situation leads to an equatorial bond angle

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[10] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

lying between 90 and 120°. On the other hand, the dipole moment (2.5 D) of $TeCl_4$ in benzene solution may be attributed to the free molecule also, and interpreted as the sum of four Te–Cl bond moments each having the value 2.3 D estimated by Smyth, Grossman and Ginsburg. For an axial–axial bond angle of 170° in the trigonal bipyramidal structure this interpretation leads to an equatorial bond angle of 102°.

The structure for $TeCl_4$ discussed here is in agreement with the prediction made by Pauling.[2] Kimball[11] suggested that $TeCl_4$ should have an "irregular tetrahedral" configuration of symmetry C_{3v}. This configuration is certainly incompatible with the results of our electron diffraction investigation; moreover, it would probably lead to a dipole moment much smaller than that found by Smyth, Grossman and Ginsburg. Kimball apparently assumed that in $TeCl_4$ the unshared pair occupies a pure s orbital. This assumption apparently is incorrect.

The Te–Cl distance, 2.33 Å., is but slightly less than 2.36 Å., which is the sum of the covalent radii.

Summary

An electron diffraction study of gaseous $TeCl_4$ leads to the values 2.33 ± 0.02 Å. for the average Te–Cl distance, 3.37 ± 0.06 Å. for the only important Cl–Cl distance, and 93 ± 3° for the corresponding important bond angle. A distorted trigonal bipyramidal configuration with the unshared pair in one of the equatorial positions is compatible with these results and the known large dipole moment of the molecule. The equatorial bond angle is probably considerably less than 120°, but greater than 90°.

PASADENA, CALIFORNIA RECEIVED MARCH 18, 1940

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[11] G. E. Kimball, *J. Chem. Phys.*, **8**, 194 (1940).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 769]

On the Molecular Structure of Sulfur Dioxide

BY VERNER SCHOMAKER AND D. P. STEVENSON

In the course of investigating the electron diffraction patterns of a number of simple molecules, we have obtained photographs of sulfur dioxide which are better than those previously obtained by Cross and Brockway,[1] in these Laboratories. Inasmuch as the interpretation of the new photographs leads to slightly different and probably more reliable values for the interatomic distances than those found by Cross and Brockway, we are reporting our results.

The apparatus and technique used in this investigation have been described by Brockway.[2] The camera distance was 10.85 cm. and the electron wave length 0.0611 Å. (a_0 = 4.070 Å. assumed for gold). The photographs were taken with the pressure of the sulfur dioxide in the sample bulb at about one atmosphere.

The photographs showed seven rings of which six could be measured easily. The resulting s values $\left(s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)$ are given in Table I.

The radial distribution function,[3] curve A of the figure, was calculated according to the modified procedure recommended by Schomaker,[4] using the coefficients C_K given in Table I. The function has two peaks corresponding to an S–O distance of 1.43₅ Å., an O–O distance of 2.49 Å., and a bond angle of 121°.

TABLE I

Max.	Min.	C_K	s_0[a]	s_0[b]	s_c[c]	s_c/s_0[a]
	1	− 6	3.33	...	3.19	(0.958)[d]
1		10	5.54	5.63	5.48	(0.989)[d]
	2	−13	7.37	...	7.45	1.011
2		15	9.87	9.66	10.00	1.013
	3	−15	12.02	11.99	12.04	1.002
3		15	14.04	13.76	14.10	1.004
	4	−14	16.49	16.19	16.58	1.005
4		13	18.59	18.15	18.54	0.997
	5	−11	20.87		20.80	0.997
5		11	23.19		23.18	1.000
	6	− 7	25.33		25.13	0.992
6		6	27.50		27.58	1.003
					Average	1.002 ± 0.005

S–O = 1.002 × 1.43 = 1.43_3 ± 0.01 Å.

[a] This research.

[b] Cross and Brockway, ref. 1, S–O = 1.46 Å.

[c] From curve for model with ∠O–S–O = 120°.

[d] Omitted from average because of unreliability of measurement.

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[1] P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

[2] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[3] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[4] V. Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.