Two Independent Determinations of the Crystal and Molecular Structure of the Iodine Monochloride Complex of Pentamethylenetetrazole

**Norman C. Baenziger,[1a] A. Dwayne Nelson,[1a]
A. Tulinsky,[1b] John H. Bloor,[1b,c] and Alexander I. Popov[1b]**

Contribution from the Departments of Chemistry, University of Iowa, Iowa City, Iowa 52240, and Michigan State University, East Lansing, Michigan 48823. *Received June 26, 1967*

Abstract: Two independent structure determinations have been carried out on the iodine chloride complex of pentamethylenetetrazole (PMT) by the use of X-ray crystallographic techniques. The two structures agree in general and agree in particular on readily determined parameters (involving iodine and/or chlorine). Thus, the PMT acts as a unidentate ligand with the iodine of ICl bound to N(2) of the tetrazole ring, the N···I–Cl group is linear and coplanar with the tetrazole ring which is itself planar, and the seven-membered ring of PMT is in a chair conformation. The results of the independent determinations are compared with respect to one another and other related molecules.

It has been shown in several publications that 1,5-substituted tetrazoles and, in particular, pentamethylenetetrazole (hereafter abbreviated as PMT, $C_6H_{10}N_4$, see Figure 1) behave as relatively strong electron donors. A solid addition compound PMT·ICl has been prepared,[2] and the formation constant of this complex was determined in carbon tetrachloride solutions. Corresponding complexes with iodine bromide and iodine could not be isolated in the solid state but their existence in solutions was shown by spectrophotometric techniques and their formation constants were likewise determined. Recently, transition metal complexes of PMT, of the type $M^{II}(PMT)_6(ClO_4)_2$, where M^{II} = Fe, Mn, Co, Ni, and Zn, have also been reported.[3]

It appears that in all of the above complexes PMT acts as a unidentate ligand. This leads one to conclude that either complexation with a halogen or a transition metal ion at any of the four ring nitrogens deactivates the ring toward further complexation or there is only one preferred bond site available for coordination.

It is interesting to point out that although PMT is a relatively strong electron donor toward Lewis acids such as halogens and transition metal ions, it has very little affinity for protons.[4] In fact, it has essentially no basic properties in aqueous solution and behaves only as a weak base even in acetic acid solutions.

It has been suggested that tetrazoles may form coordinate compounds through the π-electron system of the tetrazole ring.[5] A study of charge-transfer complexes of mono- and disubstituted tetrazoles with π-electron acceptors has shown that, while such complexes do exist in solutions, they are extremely unstable and are largely dissociated even in concentrated solutions.[6]

In view of the somewhat unusual donor properties of PMT, it was thought that a detailed analysis of the structure of the PMT·ICl complex would yield some information on the bonding site of the tetrazole ring. Coincidentally, the determination of the crystal structure of the PMT·ICl complex was begun quite independently in two laboratories (University of Iowa and Michigan State University) and only upon the completion of the two studies did the two groups of investigators become aware of each others' results. In the interest of brevity and to compare the independent results, both determinations are reported here. The designation of BN will refer to the authors Baenziger and Nelson and the designation of TBP will refer to the authors Tulinsky, Bloor, and Popov.

Structure Determination According to BN

Crystals of PMT·ICl recrystallized from chloroform gave yellow prisms. Since the crystals appeared to sublime at room temperature, a crystal (0.3 × 0.3 × 0.4 mm) sealed in a thin-walled glass capillary was used to obtain the intensity data. Precession film intensity data (Mo Kα), *hk*0 to *hk*5 and *h*0*l* to *h*5*l*, were estimated visually and 844 independent reflections were observed. Lorentz-polarization corrections were made, but absorption corrections were not applied ($\mu < 1$ cm^{-1}). The unit cell dimensions determined from back-reflection Weissenberg diagrams by a least-squares extrapolation method gave $a = 13.087 \pm 0.002$, $c = 8.339 \pm 0.002$ A. The *b* cell dimension determined from precession diagrams is less accurately known: $b = 18.83 \pm 0.02$ A. From the systematic absences the space group is Pbca.

A three-dimensional Patterson map revealed the I–Cl group. Using the position parameters for I and Cl ($R = 0.28$), the positions of the nonhydrogen atoms in the molecule were obtained from a three-dimensional electron density difference map. Least-squares refinement proceeded through steps using first isotropic temperature factors and then anisotropic temperature factors. (Atom scattering factors were the neutral atom value[7] corrected for dispersion.) The weighting scheme used was $w^{1/2} = 1/s_F$ where s_F is the standard

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[1] (a) University of Iowa; (b) Michigan State University; (c) National Science Foundation Undergraduate Participant, 1965–1966.

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Table I. Atom Parameters[a] (Values × 10^4)

	Atomic Coordinates					
	TBP			BN		
	x	y	z	x	y	z
I	1403 (1)	1517 (1)	2060 (2)	1403 (1)	1518 (1)	2059 (2)
Cl	2792 (6)	2095 (4)	3514 (10)	2785 (5)	2093 (4)	3546 (14)
C_1	4628 (26)	3818 (18)	0726 (43)	4624 (18)	3827 (12)	771 (35)
N_2	17 (20)	1026 (13)	707 (32)	13 (17)	1023 (12)	674 (31)
N_3	4416 (26)	498 (17)	3609 (45)	4370 (17)	480 (11)	3778 (37)
N_4	3665 (24)	334 (17)	4622 (41)	3647 (14)	354 (11)	4676 (39)
N_5	3798 (25)	4226 (17)	985 (42)	3767 (18)	4209 (11)	954 31)
C_6	3138 (25)	4244 (18)	2348 (45)	3040 (18)	4215 (13)	2265 (45)
C_7	3676 (33)	4409 (23)	3855 (56)	3630 (23)	4411 (13)	3778 (39)
C_8	4255 (28)	3798 (20)	4517 (45)	4310 (24)	3792 (13)	4528 (33)
C_9	237 (28)	3607 (18)	1436 (48)	284 (18)	3598 (15)	1391 (47)
C_{10}	46 (28)	3282 (18)	3144 (43)	−18 (17)	3307 (14)	3110 (41)

	Thermal Parameters[b]											
	TBP						BN					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	46	17	9	0	4	−4	73	21	116	0	2	−2
Cl	70	33	99	−8	−50	−7	100	45	224	−11	−72	9
C_1			2.11[c]				54	5	63	2	45	22
N_2			1.82[c]				110	32	48	16	56	4
N_3			3.69[c]				67	24	189	−14	72	12
N_4			3.27[c]				15	24	305	−5	6	−8
N_5			3.83[c]				102	10	200	−19	−53	14
C_6			1.90[c]				47	31	226	−11	13	−72
C_7			3.97[c]				109	20	30	3	−69	2
C_8			2.71[c]				112	19	43	6	121	−4
C_9			2.45[c]				51	54	333	−21	11	−148
C_{10}			2.29[c]				44	35	183	0	−47	−30

[a] Standard deviations in the last significant digits are given in parentheses. [b] $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [c] Isotropic thermal parameter, $B = 8\pi^2\mu^{-2}$.

deviation in the mean of all the repeated intensity estimates of each reflection. The final R factor is 0.07. An attempt was made to distinguish between the C and N atoms in the tetrazole ring. Both choices of the C atom location (refined with isotropic temperature factors) gave insignificantly different R values, but one choice gave more normal isotropic temperature factor values (2.4 A^2 for C and 4.3 A^2 for N for the positions selected as correct as compared to 0.95 A^2 for C and 4.4 A^2 for N for those positions considered incorrect). The choice appears to be clear since similar indications were obtained by TBP.[8]

Structure Determination According to TBP

Crystals of PMT·ICl grown by slow cooling of chloroform solutions were orthorhombic (a = 13.06 ± 0.02, b = 18.78 ± 0.02, c = 8.34 ± 0.01 A), space group Pbca, with eight molecules per unit cell (d_{calcd} = 1.58 g cm^{-3}). Three-dimensional intensity data (Cu Kα) were collected to 1-A resolution ($2\theta_{\max}$ = 100°) from a crystal enclosed in a glass capillary with a GE XRD-5 equipped with a scintillation counter assembly using the balanced filter, stationary crystal–stationary counter technique. Upon data reduction to structure amplitudes, the intensities were also corrected approximately for absorption and a general fall-off with X-ray exposure of the crystal. A total of 851 reflections were intense enough to be measured.

The coordinates of ICl were determined from the Harker sections of a three-dimensional sharpened

Table II. Bond Distances and Angles[a]

	TBP	BN	Average
	Bond Distance, A		
I–Cl	2.44 (1)	2.442 (9)	2.44
N_2–I	2.32 (3)	2.37 (2)	2.34
C_1–N_2	1.33 (5)	1.32 (4)	1.33
N_2–N_3	1.39 (5)	1.38 (3)	1.39
N_3–N_4	1.33 (5)	1.23 (4)	1.28
N_4–N_5	1.42 (5)	1.35 (4)	1.38
C_1–N_5	1.35 (5)	1.34 (3)	1.34
N_5–N_6	1.43 (6)	1.45 (4)	1.44
C_6–C_7	1.47 (6)	1.52 (5)	1.50
C_7–C_8	1.48 (6)	1.59 (4)	1.54
C_8–C_9	1.55 (6)	1.53 (4)	1.54
C_9–C_{10}	1.57 (6)	1.58 (5)	1.58
C_{10}–C_1	1.48 (6)	1.43 (4)	1.46
	Angle, deg		
Cl–I–N_2	177 (5)	176 (4)	177
I–N_2–C_1	130 (5)	130 (3)	130
I–N_2–N_3	122 (5)	126 (2)	125
N_3–N_2–C_1	108 (6)	104 (6)	106
N_2–N_3–N_4	109 (6)	113 (5)	111
N_3–N_4–N_5	107 (6)	106 (5)	106
N_4–N_5–C_1	108 (6)	109 (7)	108
N_4–N_5–C_6	123 (6)	121 (5)	122
C_6–N_5–C_1	129 (6)	130 (2)	129
N_5–C_6–C_7	113 (6)	107 (3)	110
C_6–C_7–C_8	114 (7)	116 (4)	115
C_7–C_8–C_9	114 (7)	116 (3)	115
C_8–C_9–C_{10}	115 (7)	109 (2)	111
C_9–C_{10}–C_1	112 (6)	116 (4)	113
C_{10}–C_1–N_2	125 (6)	128 (8)	126
C_{10}–C_1–N_5	126 (6)	124 (5)	125
N_5–C_1–N_2	109 (6)	107 (3)	108

[a] Estimated standard deviations in last significant digit are given in parentheses.

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(8) When isotropic thermal parameter refinement was commenced by TBP, these atoms were both included as carbon with B = 2.0 A^2. Upon one cycle of refinement, the thermal parameter of one atom changed to 1.68 A^2 while that of the other changed to −0.7 A^2. The latter atom was included as a nitrogen in all subsequent calculations.

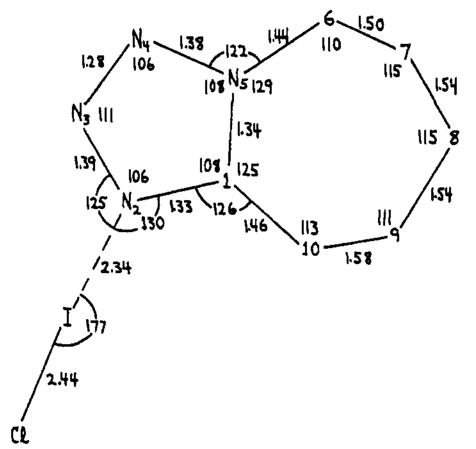

Figure 1. Average bond distances and bond angles of PMT·ICl.

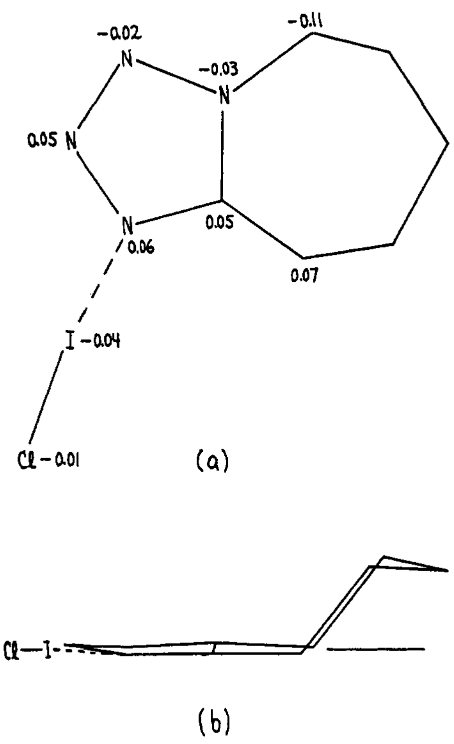

Figure 2. (a) Average out-of-plane distances (A) from least-squares plane of tetrazole ring and adjoining two carbons and ICl; standard error = ±0.06 A; all atoms included with equal weight. (b) Side view of PMT·ICl indicating chair conformation of seven-membered ring of PMT.

Patterson function and confirmed in general positions. These coordinates and an isotropic thermal parameter for each atom were refined three cycles by the method of least squares along with a scale factor ($R = 0.23$). Phases based on ICl were then employed to compute a three-dimensional difference density map subtracting ICl from the observed structure. The difference density revealed the PMT molecule unambiguously. The complete structure was then refined by the method of least squares with a weighting scheme based on that of Hughes[9] using anisotropic thermal parameters for ICl only, since the complete structure was somewhat insensitive to the PMT contribution.[10] Refinement converged with $R = 0.096$.

Discussion of the Structure

A sketch of the molecule is shown in Figure 1 in which the bond distances and angles are based on the average value of the two sets of coordinates from the independent structure determinations (cell dimensions of TBP were used for these calculations). A comparison of individual atom parameters, bond distances, and bond angles is given in Tables I and II.

The features of the structure which are clear are: (1) the PMT acts as a unidentate ligand with N(2) being involved in the bonding, (2) the N · · · I–Cl group is linear (bond angle, 177°) with an I–Cl distance of 2.44 A and an I · · · N distance of 2.34 A, (3) the I–Cl is essentially coplanar with the tetrazole which itself is planar (see Figure 2a), and (4) the seven-membered ring of PMT is in a chair conformation (see Figure 2b).

The bonding of the ICl group to N(2) of the tetrazole ring suggests that only one preferred bonding site is available for coordination. This is supported by the structure of the dichlorobis(1-methyltetrazole)zinc(II) complex where a similar situation obtains.[11] Furthermore, the ICl group is coplanar with the tetrazole which indicates that the bonding is not of a π-electron type and this is further supported by the structure of the dichlorobis(1-methyltetrazole)zinc(II) complex, where the zinc atom is approximately tetrahedral but coplanar with the tetrazole rings.[11]

The linear arrangement agrees well with structures of ICl and I_2 with pyridine and trimethylamine.[12] The I–Cl distance can be placed in the proper perspective by noting that the distance found for ICl in the vapor phase is 2.303 A;[13] the covalent radius sum (1.34 + 0.99) is 2.33 A;[14] the distances found in α- and β-ICl are 2.37, 2.44 A and 2.35, 2.44 A;[15,16] in pyridine and trimethylamine complexes the I–Cl distance is 2.52 and 2.54 A,[12] and in the ICl_2^- ion it is 2.55 A.[16]

The N–I distance found to be 2.30 A in the trimethylamine–ICl complex[10] and 2.26 (2.30 A) in the pyridine–ICl complex[12] is shorter than that observed here, 2.34 A. The distances are compatible with a donor–acceptor complex in which the transfer of charge from nitrogen to the ICl group is not as complete in the tetrazole complex as for pyridine or trimethylamine. The relative shift of the I–Cl vibrational frequency upon complexation and the respective formation constants of tetrazole and pyridine complexes with ICl are in qualitative agreement.[17]

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[10] Upon including PMT into structure factor calculations, R changed from 0.23 to 0.20; however, further refinement of ICl (isotropic) of this structure reduced R to 0.14. The remainder of the improvement in agreement came essentially from anisotropic thermal parameters on ICl.

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