1,2,4-Triazines XIII. The Bond Lengths and Bond Angles of a 1,2,4-Triazine

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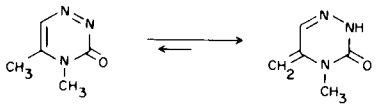
The bond distances and bond angles of 5-(*p*-chlorophenyl)-1,2,4-triazine determined by three dimensional X-ray crystallographic analysis are reported. The pertinent bond lengths are N_1-N_2, 1.335Å, N_2-C_3, 1.314Å, C_3-N_4, 1.339; N_4-C_5, 1.317; C_5-C_6, 1.401; C_6-N_1, 1.317Å. A comparison of these bond distances with those of similar polyazabenzenes shows that the canonical structure of 1,2,4-triazine with a N_1-N_2 single bond more closely represents the ground state of this ring system, than the one with a N_1-N_2 double bond.

Since our original synthesis of the parent 1,2,4-triazine (**1**) (1), we have been concerned with the study of the chemistry of this ring system.

1

These studies have brought to light the fact that 1,2,4-triazines readily undergo covalent hydration across the N_4-C_5 bond (2), are subject to H_3-D_3 exchange under neutral as well as basic conditions (3); can be *N*-oxidized at N_1 if C_3 is either unsubstituted or contains a methylthio or methoxyl grouping, or at N_2 if C_3 is substituted by an amino group (4). Furthermore, in derivatives (e.g. **2**), where an -N=N- would be forced it is removed by tauto-



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merization (e.g. **3**) (5). Neuenhoeffer, (6), and others (7), have also shown that 1,2,4-triazines can act as dienes in Diels-Alder reactions.

On the "theoretical side" of 1,2,4-triazine chemistry, a paper by Dewar and Gleicher (8) has examined various parameters in calculations of the SPO and PPP type. These calculations have led to the calculated bond distances reported in Table I.

We now wish to report the crystal structure, determined from three-dimensional X-ray data, for 5-(*p*-chlorophenyl)-1,2,4-triazine (**4**) (9). The dimensions obtained for the 1,2,4-triazine ring system of this compound are not expected to be significantly different from that of the parent 1,2,4-triazine.

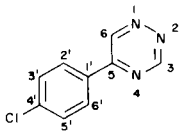

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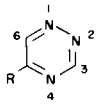
Table I

Experimental and Calculated Bond Distances of 1,2,4-Triazine



Bond	Exptl (a)	PPP (8,b)	SPO (8,b)
1-2	1.335	1.335	1.348
2-3	1.314	1.310	1.304
3-4	1.339	1.361	1.357
4-5	1.317	1.304	1.298
5-6	1.401	1.443	1.460
6-1	1.317	1.297	1.289

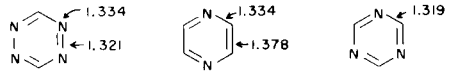
(a) All values are in Å, determined for R = *p*-ClC_6H_5-. Standard deviations are 0.004Å. (b) Data for R = H.

The bond lengths obtained for this molecule will not only allow the first comparison of experimentally determined bond length of 1,2,4-triazine with those calculated by semiempirical molecular orbital calculations, but also shed some light upon the chemical properties of this molecule in comparison with other polyazabenzenes.

When the bond lengths obtained by the PPO and SOP calculations (*cf.* Table I) are compared with the experimentally determined bond distances, the correlation be-

tween these values is indeed remarkable when one considers the numerous approximations employed in these semi-empirical calculations.

It is instructive to compare the bond lengths and bond angles of 1,2,4-triazine with those of some other polyazabenzenes (10,11,12) (**5**, **6**, **7**):



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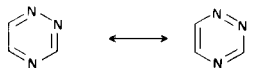
These compounds are unique, with respect to 1,2,4-triazine, in that the two canonical structures contributing to the ground state of each are identical. This identity does not apply to the two "canonical" structures, **8** and **9**, of the 1,2,4-triazine ring system, where structure **8** has a formal



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N-N single bond, while structure **9** has a formal N-N double bond, for example. Consideration of these two structures in terms of the lone-pair of electrons repulsion between N_1 and N_2 suggests that the N-N single bond structure **8** should be more stable than the N-N double bond structure **9**. Thus, the N-N bond length in 1,2,4-triazine should be longer than the similar bonds (N_1-N_2 and N_4-N_5) in 1,2,4,5-tetrazine (**5**). Furthermore, the C_3-N_4 distance in 1,2,4-triazine should be considerably longer than the N_1-C_2 length in 1,3,5-triazine (**7**). Similarly, the C_5-C_6 length in 1,2,4-triazine should also be longer than the C_2-C_3 bond distance in pyrazine (**6**). On the other hand, the N_2-C_3, N_4-C_5 and N_1-C_6 bond length in the 1,2,4-triazine **4** should all be shorter than the comparable N_1-C_2 length in 1,2,4,5-tetrazine (**5**), pyrazine (**6**) and the N_2-C_3 length in 1,2,4,5-tetrazine (**5**), respectively.

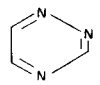
Table II shows that all of these predictions are borne out by the experimental results on the 1,2,4-triazine compound

Table II

Bond Lengths Comparisons of Some Polyazabenzenes

Bond Designation	Compound (No.)	Bond Length (A°)
N_1-N_2	1,2,4-triazine (**4**)	1.335
N_1-N_2	1,2,4,5-tetrazine (**5**)	1.321
C_3-N_4	1,2,4-triazine (**4**)	1.339
N_1-C_2	1,3,5-triazine (**7**)	1.319
C_5-C_6	1,2,4-triazine (**4**)	1.401
C_2-C_3	pyrazine (**6**)	1.378
N_2-C_3	1,2,4-triazine (**4**)	1,314
N_1-C_2	1,2,4,5-tetrazine (**5**)	1.334
N_4-C_5	1,2,4-triazine (**4**)	1.317
N_1-C_2	pyrazine (**6**)	1.334
N_1-C_6	1,2,4-triazine (**4**)	1.317
N_2-C_3	1,2,4,5-tetrazine (**5**)	1.334

4. Since one cannot obtain appropriate bond lengths for a non-delocalized 1,2,4-triazine structure, such as **10**, it is impossible to make a reasonably quantitative assessment as



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to the "percentage" contribution of canonical structures **8** and **9** to the ground state of 1,2,4-triazines. Nevertheless, the previous analysis allows us to state that the 1,2,4-triazine structure should be written as **8** since this contributor makes a greater contribution to the ground state than does canonical structure **9**. The data (*cf.* Experimental Section) also establish that compound **4** is planar to within 0.01Å, an observation to be expected for an aromatic system.

Table III

Crystal Data for 5-(*p*-Chlorophenyl)-1,2,4-triazine

Mol formula: $N_3C_9H_6Cl$
Mol wt: 186.6
Linear abs coeff μ: 4.14
Crystal size: spherical, radius of 0.20 mm
Space group: monoclinic, Pz_1/n
Molecules/unit cell: 4
Cell constants (a): a = 7.578(6), b = 7.542(6), c = 15.417(9)Å, β = 92.62(6)°
Calculated density: 1.48 g./cm^3
Observed density: 1.48 g./cm^3
Cell vol: 880.2Å^3

(a) MoKα radiation, λ = 0.71069Å. Ambient temperature of 26 ± 1°.

EXPERIMENTAL

X-Ray Data Collection.

Final unit cell parameters as determined from a least-squares refinement of the angular settings of 12 reflections accurately centered on an ENRAF-NONIUS CAD-4 diffractometer are given in Table III. Data were taken on the diffractometer with graphite crystal monochromated molybdenum radiation. The crystal was aligned such that no symmetry axis was coicident with the ϕ axis of the diffractometer. The diffracted intensities were collected by the ω-2θ scan technique with a take-off angle of 3.5°. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0.3° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation where A = 1.0°

$$\text{scan range} = A + B \tan \theta$$

and B = 0.5°. Aperture settings were determined in a like manner with A = 4mm and B = 4mm. Other diffractometer parameters and

Table IV

Final Fractional Coordinates and Anisotropic Thermal Parameters (a) for Compound 4

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.0729 (12)	0.92100 (13)	0.33293 (6)	256 (2)	294 (2)	73 (0)	17 (2)	-20 (1)	7 (1)
C (1)	0.1438 (4)	0.7520 (4)	0.4034 (2)	144 (6)	209 (6)	50 (2)	-5 (5)	-7 (2)	34 (3)
C (2)	0.1861 (4)	0.5895 (5)	0.3712 (2)	202 (6)	264 (8)	32 (1)	-4 (6)	-4 (2)	11 (3)
C (3)	0.2450 (4)	0.4575 (4)	0.4283 (2)	203 (6)	192 (6)	32 (1)	4 (5)	-1 (2)	-5 (2)
C (4)	0.2566 (3)	0.4896 (3)	0.5179 (2)	130 (5)	153 (5)	29 (1)	-14 (4)	5 (2)	-2 (2)
C (5)	0.2094 (4)	0.6550 (4)	0.5480 (2)	189 (6)	180 (6)	39 (1)	9 (5)	2 (2)	-3 (2)
C (6)	0.1537 (4)	0.7877 (4)	0.4912 (2)	207 (6)	177 (6)	53 (2)	25 (5)	-2 (3)	7 (3)
C (7)	0.3194 (3)	0.3485 (3)	0.5784 (2)	129 (5)	145 (5)	30 (1)	-21 (4)	4 (2)	-3 (2)
C (8)	0.4426 (4)	0.0813 (4)	0.6053 (2)	219 (7)	171 (6)	46 (1)	12 (5)	-1 (2)	8 (3)
C (9)	0.3111 (4)	0.3646 (4)	0.6686 (2)	268 (7)	209 (6)	31 (1)	33 (6)	6 (2)	0 (2)
N (1)	0.3843 (3)	0.2012 (3)	0.5467 (1)	209 (5)	170 (5)	33 (1)	5 (4)	-1 (2)	-4 (2)
N (2)	0.4401 (3)	0.0937 (3)	0.6903 (1)	224 (6)	216 (6)	44 (1)	-0 (5)	-2 (2)	22 (2)
N (3)	0.3699 (4)	0.2405 (4)	0.7226 (1)	297 (7)	251 (6)	34 (1)	25 (5)	2 (2)	11 (2)
H (1)	0.189 (4)	0.566 (5)	0.308 (2)	(b)					
H (2)	0.280 (4)	0.341 (5)	0.407 (2)						
H (3)	0.209 (4)	0.679 (5)	0.612 (2)						
H (4)	0.120 (4)	0.902 (5)	0.514 (2)						
H (5)	0.498 (4)	-0.031 (5)	0.583 (2)						
H (6)	0.254 (4)	0.464 (5)	0.696 (2)						

(a) Anisotropic thermal parameters x 10^4 defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$. (b) Hydrogen atoms were assigned an isotropic temperature factor of 5.0.

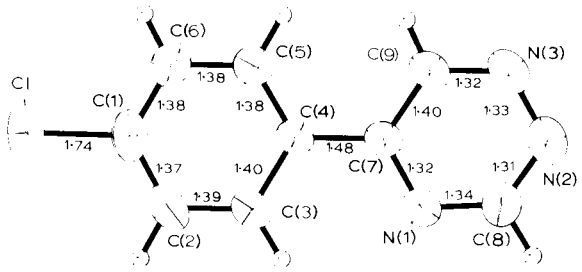

Figure 1.

Molecular Structure of 5-(*p*-Chlorophenyl)-1,2,4-triazine with the Atoms Displayed as 50% Probability Ellipsoids for Thermal Motion.

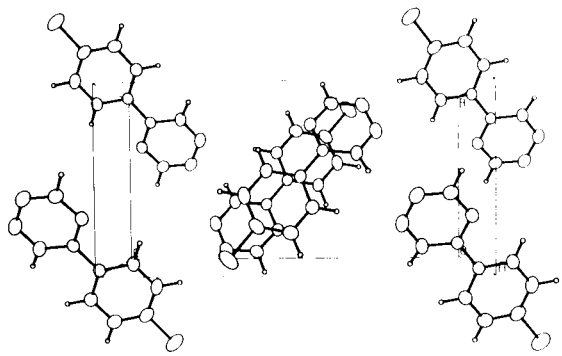

Figure 2.

Unit Cell Packing of 5-(*p*-Chlorophenyl)-1,2,4-triazine Viewed Down the *a* Axis.

the method of estimation of standard deviations have been described previously (13). As a check on the stability of the instrument and the crystal, three reflections, the (200), (20$\bar{2}$), and (01$\bar{2}$), were measured after every 30 reflections; no significant variation was noted.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1037 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 1037 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$.

The intensities were corrected for Lorentz and polarization effects, but not for absorption, since $\mu = 4.14$.

Fourier calculations were made with the ALFF (14) program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS (15). The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous disperison. Neutral atom scattering factors were taken from the compilations of Cromer and Waber (16) for Cl, N, and C; those for hydrogen were from "International Tables for X-ray Crystallography" (17). Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program (18). Crystal structure illustrations were obtained with the program ORTEP (19).

Structure Solution and Refinement.

The chlorine atom position was determined from the Patterson map, and subsequent electron density calculations revealed the coordinates of all non-hydrogen atoms in the asymmetric unit. Anisotropic least-squares refinement with unit weights led to agreement indices of 0.053 and 0.051, respectively. Location and refine-

$$R_1 = \Sigma\, |F_o| - |F_c| \,/\, \Sigma\, |F_o|$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 \,/\, \Sigma w\, |F_o|^2]^{1/2}$$

ment of hydrogen atom coordinates followed by further cycles of anisotropic refinement of the non-hydrogen atoms gave final values of $R_1 = 0.039$ and $R_2 = 0.034$. Unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference Fourier map showed no feature greater than $0.3e^-/Å^3$. The final values of the positional and thermal parameters are given in Table IV (20).

The equation of the plane of the 1,2,4-triazine ring is -0.9049X -0.4244Y -0.0327Z + 3.2154 = 0, and all six atoms are planar to within 0.01 Å.

Table V

Bond Distance (Å) and Angles (°) of Compound **4**

Bond Distances

Cl - C(1)	1.744 (3)	N(2) - N(3)	1.335 (4)
C(1) - C(2)	1.366 (4)	N(1) - C(7)	1.317 (3)
C(2) - C(3)	1.389 (4)	N(2) - C(8)	1.314 (4)
C(3) - C(4)	1.401 (3)	N(3) - C(9)	1.317 (4)
C(4) - C(5)	1.384 (4)	N(1) - C(8)	1.339 (3)
C(5) - C(6)	1.383 (4)	C(7) - C(9)	1.401 (4)
C(6) - C(1)	1.378 (4)	C(4) - C(7)	1.480 (3)
C(2) - H(1)	0.99 (4)	C(3) - H(2)	0.98 (4)
C(5) - H(3)	1.00 (4)	C(6) - H(4)	0.97 (4)
C(8) - H(5)	1.01 (4)	C(9) - H(6)	0.97 (4)

Bond Angles

Cl - C(1) - C(2)	120.0 (2)	C(5) - C(4) - C(7)	121.2 (3)
Cl - C(1) - C(6)	118.1 (2)	C(4) - C(7) - N(1)	119.2 (2)
C(1) - C(2) - C(3)	119.1 (3)	C(4) - C(7) - C(9)	122.4 (2)
C(2) - C(3) - C(4)	120.3 (3)	C(7) - N(1) - C(8)	115.9 (2)
C(3) - C(4) - C(5)	118.8 (3)	N(1) - C(8) - N(2)	127.2 (3)
C(4) - C(5) - C(6)	121.0 (3)	C(8) - N(2) - N(3)	117.1 (2)
C(5) - C(6) - C(1)	118.8 (3)	N(2) - N(3) - C(9)	118.8 (2)
C(6) - C(1) - C(2)	122.0 (3)	N(3) - C(9) - C(7)	122.5 (3)
C(3) - C(4) - C(7)	120.1 (2)	C(9) - C(7) - N(1)	118.4 (2)

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(20) A complete table of the observed and calculated structure factors is available upon request.