Conformation Analysis. 6. The Molecular Structure of Gaseous Tetrabromoformaldazine as Determined by Electron Diffraction

Kolbjørn Hagen, Vladimir Bondybey, and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received March 16, 1978

Abstract: The structure of gaseous tetrabromoformaldazine ($Br_2CNNCBr_2$) has been investigated by electron diffraction at a nozzle-tip temperature of 112 °C. In contrast to formaldazine itself which exists in two conformations, the tetrabromo compound was found only in a single, nonplanar form. The data were fit well by a model of C_2 symmetry with planar $NCBr_2$ groups, a torsion angle CNNC equal to 72.1° (5.2) relative to 0° for the planar anti form, and a torsion around the double bond NNCBr equal to 16.6° (3.9) taken in such a sense as to increase the separation between an unshared nitrogen electron pair and the bromine atom syn to it in the adjacent $NCBr_2$ group. Other geometrical parameter values with uncertainties estimated at 2σ are $r(C–Br) = 1.877$ Å (0.005), $r(N–N) = 1.381$ Å (0.018), $r(C=N) = 1.266$ Å (0.008), $\angle CNN = 114.5°$ (1.6), and $\angle NCBr = 126.2°$ (1.0) and 118.2° (1.1) where the last two angles correspond to a rocking displacement of the CBr_2 group away from the nitrogen atom of the adjacent $NCBr_2$ group. The conformation is discussed in comparison with similar molecules.

Our recent investigation of the structure of gaseous formaldazine[1] (2,3-diaza-1,3-butadiene) revealed that the molecule existed as a mixture of two rotational conformers, a more stable anti ($\phi = 0$) form and a less stable gauche ($\phi = 120°$) form. Replacement of the hydrogen atoms in formaldazine with much larger atoms such as bromine would be expected to create larger steric interactions between the terminal (bromine) atoms and the lone-pair electrons on the nitrogen atoms in a possible anti conformer, and between bromine atoms on opposite ends of the molecule in a gauche or syn conformer. Such interactions would clearly play an important role in determining both the nature and the relative amounts of conformers of the molecule. No structure information has so far been reported for tetrabromoformaldazine and we decided to study it in connection with our program of work on the structures and compositions of conjugated systems.

Experimental Section

Tetrabromoformaldazine was prepared as described by Thiele[2] and was purified by recrystallization from glacial acetic acid. It had a melting point of 42 °C as reported,[2] and sufficient vapor pressure for the electron diffraction experiment was obtained by heating the sample to 95 °C. Electron-diffraction photographs were made in the Oregon State apparatus at a nozzle-tip temperature of 112 °C under conditions very similar to those described for formaldazine.[1] Photographs were made at two nozzle-to-plate distances, 29.986 and 74.983 cm, and four plates from each of the two distances were selected for use in the analysis. The ranges of data from these distances were $2.00 \leq s \leq 11.75$ Å^{-1} and $8.00 \leq s \leq 29.00$ Å^{-1}, respectively ($s = 4\pi\lambda^{-1}\sin\theta$, where λ is the electron wavelength and 2θ is the scattering angle). The forms of the mathematical functions and the general methods used in the analysis have been described.[3-5] The elastic and inelastic electron-scattering amplitudes and phases were obtained from tables.[6] A composite curve of the experimental intensity is shown in Figure 1, and the corresponding radial distribution curve is shown in Figure 2.

Structure Analysis

The origins of the various peaks in the experimental radial distribution curve may be deduced by referring to the atom numbering in Figure 3 and the labeled vertical lines on the theoretical curve. The experimental curve showed that the molecular conformation of lowest energy could not be planar anti as in formaldazine. Theoretical radial distribution curves calculated for models with different CNNC torsional angles gave the best fit when the torsional angle had values in the range 70-90° relative to 0° for the planar anti form. Rather

unexpectedly, however, we were unable to obtain satisfactory fits without also introducing a small twist around the carbon–nitrogen double bonds in such a sense as to continue to increase the separations between the unshared nitrogen electron pairs and the bromine atoms originally syn to them. This type of model (having C_2 symmetry) was accordingly adopted for refinement.

Refinements of the structure were carried out by the method of least squares based on intensity curves,[7] adjusting a single theoretical curve to the eight sets of data simultaneously, using a unit weight matrix. Assuming only one conformation of C_2 symmetry and equal C–Br distances, the geometry of tetrabromoformaldazine can be defined by eight parameters, chosen for our refinements to be $r(C=N)$, $r(N–N)$, $r(C–Br)$, $\angle CNN$, $\langle\angle NCBr\rangle = (\angle N_1C_2Br_4 + \angle N_1C_2Br_3)/2$, $\Delta(\angle NCBr) = \angle N_1C_2Br_4 - \angle N_1C_2Br_3$, $\angle CNNC$, and $\angle NNCBr$. The 15 different amplitudes of vibration were reduced to 10 parameters by forming the groups $l(N–N) = l(C=N) + \Delta_1$, $l(C–Br)$, $l(C_2 \cdots N_5)$, $l(N_1 \cdots Br_3) = l(N_1 \cdots Br_4) = l(N_1 \cdots Br_8)$, $l(Br_3 \cdots Br_4)$, $l(C_2 \cdots C_6) = l(C_2 \cdots Br_8)$, $l(C_2 \cdots Br_7)$, $l(Br_3 \cdots Br_7)$, $l(Br_3 \cdots Br_8)$, and $l(Br_4 \cdots Br_8) = l(N_1 \cdots Br_7) + \Delta_2$, with Δ_i assumed constants. The amplitudes of vibration for the carbon–nitrogen and the nitrogen–nitrogen bonds could not be determined by refinements and they were therefore assigned reasonable values. All other amplitude and geometrical parameters were refined simultaneously. Shrinkage corrections were ignored.

Final Results and Discussion

The final results of our refinements are given in Table I and the correlation matrix for the geometrical parameters in Table II; the complete correlation matrix is available as supplementary material. Intensity and radial distribution curves together with difference curves are shown in Figures 1 and 2.

Although the model portrayed by the values of Table I is on the whole a reasonable one, some of its features need to be regarded with a certain amount of caution. For example, it must not be assumed that we have *proven* there exists a slight twist about the carbon–nitrogen double bond. Our model assumes planarity of the Br_2CN groups and neglects shrinkage corrections. Inclusion of these corrections would probably change both torsion-angle values slightly, and relaxation of the planarity assumption would make even the definition of the torsion about the carbon–nitrogen bonds somewhat obscure. Since,
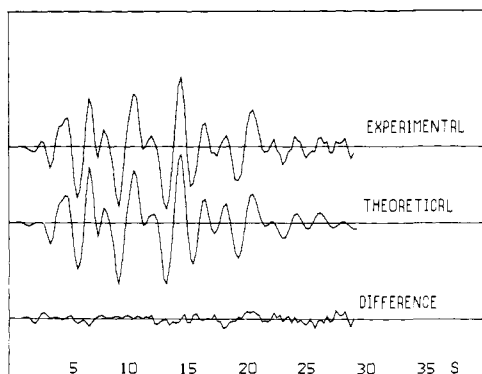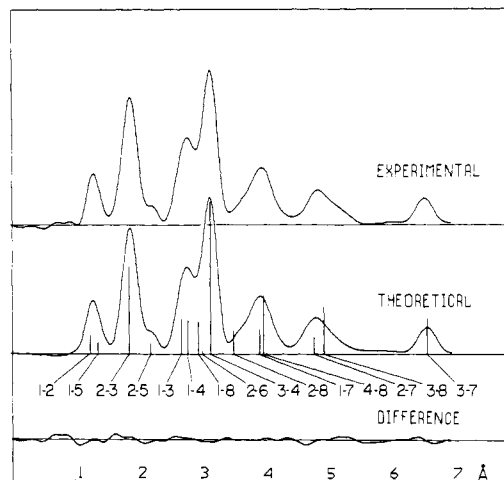
Figure 1. Intensity curves for tetrabromoformaldazine. The experimental curve is a composite from several experiments; the theoretical curve was calculated from the parameter values of Table I. The curves are in the form $sI_m(s)$ (see ref 7).

**Table I.** Final Structural Parameters for Tetrabromoformaldazine[a]

parameter	r_a	$2\sigma^b$	l^c	$2\sigma^b$
C=N	1.266	0.008	(0.0400)	
N-N	1.381	0.018	(0.0450)	
C-Br	1.877	0.005	0.072	0.007
∠CNN	114.5	1.6		
⟨∠NCBr⟩	122.2	0.2		
Δ(∠NCBr)	8.0	2.0		
∠NNCBr	16.6	3.9		
∠CNNC	72.1	5.2		
dependent parameters				
$C_2 \cdots N_5$	2.227	0.015	0.060	0.017
$N_1 \cdots Br_3$	2.715	0.013	0.089	
$N_1 \cdots Br_4$	2.817	0.017	0.089	0.018
$N_1 \cdots Br_8$	2.986	0.022	0.089	
$Br_4 \cdots Br_8$	4.020	0.084	0.205	0.020
$N_1 \cdots Br_7$	3.966	0.021	0.115	
$Br_3 \cdots Br_4$	3.175	0.006	0.094	0.005
$C_2 \cdots C_6$	3.063	0.029	0.157	0.054
$C_2 \cdots Br_8$	3.553	0.050	0.157	
$C_2 \cdots Br_7$	4.816	0.029	0.127	0.041
$Br_3 \cdots Br_7$	6.612	0.024	0.136	0.020
$Br_3 \cdots Br_8$	4.993	0.083	0.250	0.074
$∠N_1C_2Br_4$	126.2	1.0		
$∠N_1C_2Br_3$	118.2	1.1		
R^d	0.24			

[a] Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. [b] 2σ includes estimates of systematic errors and the effect of correlation. See ref 13. [c] Bracketed quantities were refined as a group; parenthesized values were assumed. [d] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i I_i(\text{obsd})^2]^{1/2}$ where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$.

as discussed below, the two symmetrically nonequivalent sets of bromine atoms are surely subject to rather different steric forces making strict planarity of the Br_2CN groups unlikely, we prefer to regard our model of Table I only as one *consistent* with the diffraction data. We did not investigate the effect of nonplanarity of the groups mentioned because electron-diffraction patterns are rather insensitive to small deformations of this type and it seemed certain that no unambiguous conclusions could be reached. Nor did we investigate shrinkage corrections which are uncertain in any case without a reasonable force field on which to base their calculation. In summary, we feel that although the precise values of the torsion angles are uncertain because of the limitations imposed by our model, the bond distances and bond angles should be relatively insensitive to these limitations and their values may be accepted with reasonable confidence.

Figure 2. Radial distribution curves for tetrabromoformaldazine. The curves were calculated from the intensity curves of Figure 1 with $B = 0.0020$. Unobserved experimental intensity data for the region $0 \leqslant s \leqslant 2.00$ A^{-1} were taken from the theoretical curve. The vertical lines indicate the interatomic distances in the final model; the lengths of the lines are proportional to the weights of the distances.
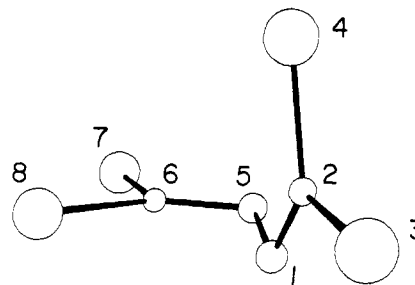
Figure 3. Diagram of the tetrabromoformaldazine molecule with atomic numbering.

The similarities between the shapes of formaldazine[1] and 1,3-butadiene[8,9] on the one hand and tetrabromoformaldazine, hexafluoro-1,3-butadiene,[10] and hexachloro-1,3-butadiene[11] on the other strongly suggest that similar effects are operating in these molecules. These effects are presumably the competing ones of conjugation tending to stabilize planar conformations and steric effects tending to destabilize them. In butadiene and in the planar form of formaldazine the steric effects are small because only small atoms (hydrogen) are found on the molecular periphery; here conjugation plays the dominant role. (Incidentally, conjugation is evidently relatively weaker in formaldazine than in butadiene since a second, less stable, gauche form is also observed for it and not for butadiene.) In the perhalo compounds significant steric repulsion between the larger peripheral atoms would be expected for planar forms. Those which would operate in the anti planar butadienes between syn halogen atoms on C_1 and C_3 and on C_2 and C_4 are relieved principally by torsion about the conjugated single bond C_2-C_3. In a planar anti tetrabromoformaldazine molecule strong steric repulsion would be expected between halogen atoms and the unshared pairs syn to them on the nitrogen atoms; as in the perhalobutadienes this repulsion would be relieved by torsion around the central bond.

The magnitudes of the torsion angles CNNC in tetrabromoformaldazine and CCCC in the perhalobutadienes are rather different: 72.1° (5.2) in $C_2N_2Br_4$, 101.9° (1.1) in C_4Cl_6, and 132.6° (0.8) in C_4F_6, all relative to the planar anti angles taken as zero. Although detailed comparisons of these values

Table II. Correlation Matrix × 100 for Geometrical Parameters of Tetrabromoformaldazine[a]

	r(N–N)	r(C=N)	r(C–Br)	∠CNN	(∠NCBr)	Δ(∠NCBr)	∠CNNC	∠NNCBr
σ^b	0.0063	0.0027	0.0015	0.57	0.08	0.35	1.82	1.37
	100	45	−16	−71	−16	45	−15	24
		100	−20	−47	−31	47	−3	12
			100	9	80	15	25	−14
				100	5	−63	53	−55
					100	−7	21	−23
						100	−8	15
							100	−87
								100

[a] Distances (r) and roof-mean-square amplitudes (l) in ångströms; angles in degrees. [b] Standard deviations from least squares.

are meaningless because of possible nonplanarity of the trigonally bonded groups comprising the ends of the molecules, the values are not inconsistant with the qualitative ideas outlined above. Calculation based on the reported geometries and on van der Waals radii shows, for example, that nonbond repulsions for a given value of central bond torsion angle have for the three molecules the relative magnitudes $C_2N_2Br_4 > C_4Cl_6 > C_4F_6$ assuming, of course, that the unshared electron pair in $C_2N_2Br_4$ plays an important repulsive role. If the gauche and anti conformations in conjugated systems of this type are taken to be ones for which *bond–bond* repulsions are minimal as we have argued in the cases of the oxalyl halides,[5,12] then the relative values of the torsion angles in the three molecules may be understood as follows. The anti forms are unstable because of the dominant effect of atom–atom steric repulsion. At the gauche conformation (torsion angle equal to 120° relative to anti at 0°) the effect of conjugation tending to stabilize the syn forms is opposed by the steric effects, least for the fluorine and greatest for the bromine compound, so as to result in the observed relative magnitudes of torsion angle.

References and Notes

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Mechanisms of Gas-Phase and Liquid-Phase Ozonolysis

Lawrence B. Harding and William A. Goddard III*

Contribution No. 5613 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received June 20, 1977

Abstract: Generalized valence bond (GVB) and configuration interaction (CI) calculations using an extensive basis [double ζ plus polarization functions (DZd)] have been carried out on peroxymethylene (H_2COO, often referred to as carbonyl oxide or as the Criegee intermediate), dioxirane, and dioxymethylene (OCH_2O). The ab initio thermochemical results are combined with existing thermochemical data to analyze possible modes of ozonolysis. The predicted heat of formation of peroxymethylene is 29.1 kcal, indicating that the dissociation of the primary ozonide to form peroxymethylene biradical and formaldehyde is 9 kcal endothermic. The ring state, dioxirane, is predicted to be 36 kcal below peroxymethylene with dioxymethylene lying 15 kcal above the ring state. Gas-phase experimental results are shown to be consistent with the predicted thermochemistry. In addition, solution-phase results on the stereospecificity of ozonolysis are shown to be consistent with a biradical intermediate.

I. Introduction

The reaction of ozone and olefins has been of continuing interest to chemists for over 100 years. Most recently the gas-phase reaction has received considerable attention due to its importance in photochemical smog formation.[2] Nearly 30 years ago Criegee proposed[3] the mechanism in order to explain the isolation of 1,2,4-trioxolanes (**3**) from ozone–olefin reaction mixtures and to explain the incorporation of foreign aldehydes into these products. Since then a great deal of experimental