X-Ray Structure Determination of Three Polycyclic cis-Azoalkanes; Consequences of the Gradual Introduction of Four-membered Rings

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The crystal structures of I, 2,3-diazabicyco-[2.2.2]-oct-2-ene; II, 7,8-diazatricyclo[4.2.2.0²·⁵]-dec-7-ene; and III, 7,8-diazapentacyclo-[4.2.2.0²·⁵.0³·⁹.0⁴·¹⁰]-dec-7-ene have been determined at −165 °C by X-ray methods using 417, 924, and 933 reflections, respectively, collected on a counter diffractometer. The crystal data are as follows:

I. Orthorhombic, space group $P2_12_12$, $a = 7.930(5)$ Å; $b = 6.580(8)$ Å; $c = 5.594(5)$ Å.

II. Monoclinic, space group $P2_1/m$, $a = 5.894(1)$ Å; $b = 10.038(3)$ Å; $c = 6.577(1)$ Å; $\beta = 113.83(2)°$.

III. Monoclinic, space group $P2_1/n$, $a = 9.249(2)$ Å; $b = 6.408(2)$ Å; $c = 10.294(2)$ Å; $\beta = 103.25(2)°$.

The structures were refined to conventional R-factors of 0.046(I), 0.042(II), and 0.059(III); the standard deviations in bond lengths and angles involving nitrogen and carbon atoms are in the ranges $0.001 - 0.004$ Å and $0.1 - 0.2°$, respectively.

The effect of the introduction of four-membered rings into the 2,3-diazabicyclo-[2.2.2]oct-2-ene structure on the molecular geometry is discussed and correlated with photoelectron spectroscopy measurements.

Although aromatic azo compounds have been of great chemical and industrial importance for the past hundred years, serious interest in the azo functionality of alkanes is a relatively recent development. In particular the availability of a wide range of cis-azoalkanes [1-3] has stimulated a host of experimental and theoretical studies.

Several of the physically oriented studies have been supplemented by semi-empirical calculations.[4-6] Lacking detailed structural information for cis-azoalkanes workers have derived molecular geometries by extrapolating data from the few trans-azo structures available,[7] from a single heavily substituted five-membered ring case,[8] and from azobenzenes.[9] Alternatively geometry/energy optimizations based on the CNDO-MO-SCF approximation have been performed.[6,10]

Given the general interest in cis-azoalkanes and the present lack of structural data for this important functional group, we have undertaken an X-ray analysis of the three polycyclic derivatives (see Fig. 1):

I. 2,3-diazabicyclo[2.2.2]oct-2-ene
II. 7,8-diazatricyclo[4.2.2.0²·⁵]dec-7-ene
III. 7,8-diazapentacyclo[4.2.2.0²·⁵.0³·⁹.0⁴·¹⁰]-dec-7-ene

EXPERIMENTAL

Compounds I and II were prepared from the corresponding semicarbazides by the cupric halide oxidation method.[3] The precursor for II-semicarbazide has been described.[11] Compound III was derived from the corresponding N-phenyl urazole polycycle.[12]

Crystals formed by sublimation (I) or recrystallization from hexane (II, III) were cut to approximately cubic forms with dimensions $0.2 - 0.4$ mm along the edges. The X-ray experiments were performed on a SYNTEX PĪ four-circle diffractometer using MoKα radiation (graphite monochromator). The temperature at the crystal site was kept at −165 °C using an Enraf-Nonius cooling device modified by H. Hope. Cell dimensions were determined

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from diffractometer measurements on 15 general reflections; the results are given together with space group data below.

Intensity data were collected using the ω scan technique for reflections up to a sin θ/λ value of 0.7 Å⁻¹ with scan speeds of $3-6°$ min⁻¹ depending on the peak intensity. Scan ranges were 1.5° for compounds I and II, and 1.3° for compound III. Background counts were taken for 0.35 times the scan time ± 1.5, ± 1.0 and ± 1.0° off the peak position, respectively, for the three compounds. Three standard reflections were measured after every 100 reflections; for the three runs of data collection they were stable within 5, 3 and 5 %. No corrections were made for these fluctuations. The estimate of the standard deviation of the intensity was based on counting statistics with an additional term of 2 % of the net intensity. Reflections with intensity larger than $2.5\sigma(I)$ were regarded as observed and used for the structure determination. The data sets were corrected for Lorentz and polarization effects, no absorption or secondary extinction corrections were carried out. The numbers of

observed reflections were 417 for compound I, 924 for compound II and 933 for compound III.

Descriptions of the computer programs applied for the structure analyses are given in Refs. 13 and 14. In the full matrix least-squares program the quantity minimized was $\sum w\Delta F^2$ where w is the inverse of the variance of the observed structure factor. Atomic form factors used were those of Doyle and Turner [15] for nitrogen and carbon and of Stewart, Davidson and Simpson [16] for hydrogen atoms.

CRYSTAL DATA

Compound I. 2,3-Diazabicyclo[2.2.2]oct-2-ene, $C_6H_{10}N_2$. Orthorhombic, $a = 7.930(5)$ Å; $b = 6.580(8)$ Å; $c = 5.594(5)$ Å; $(t = -165$ °C); $V = 291.9$ Å³; $M = 110.1$; $F(000) = 120$; $Z = 2$. $D_{calc} = 1.261$ g cm⁻³. Absent reflections: $(h00)$ for h odd; $(0k0)$ for k odd. Space group $P2_12_12$.

Compound II. 7,8-Diazatricyclo[4.2.2.0²·⁵]-

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by $\exp -2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl)$.

Compound I	x	y	z	$U_{11}(Å)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	.0545(2)	.0692(3)	.5577(3)	.0269(8)	.0302(8)	.0253(7)	.0009(7)	-.0018(6)	-.0012(7)
C5	.1794(2)	-.0427(3)	.1792(4)	.0185(7)	.0312(10)	.0272(8)	.0025(7)	.0032(8)	.0037(10)
C6	.1066(2)	.1393(3)	.3171(4)	.0215(7)	.0241(8)	.0270(9)	-.0028(7)	-.0009(8)	.0002(9)
C7	-.0529(2)	.2174(3)	.1917(4)	.0265(9)	.0244(9)	.0287(8)	.0051(8)	-.0013(9)	.0020(9)
H1C5	.293(3)	-.079(3)	.247(3)	1.9(5)					
H2C5	.198(2)	.005(3)	.004(4)	1.2(5)					
HC6	.187(3)	.244(3)	.339(4)	2.3(5)					
H7C7	-.020(2)	.259(3)	.027(3)	1.4(4)					
H2C7	-.099(3)	.333(4)	.282(4)	2.6(5)					
Compound II									
N1	.0309(2)	.3125(1)	.0836(2)	.0209(4)	.0313(5)	.0284(4)	.0030(3)	.0117(3)	.0057(3)
C5	.3781(2)	.3263(1)	-.0258(2)	.0232(4)	.0340(5)	.0219(4)	.0006(4)	.0109(3)	.0063(4)
C6	.2795(2)	.3751(1)	.1442(2)	.0225(4)	.0195(4)	.0270(5)	.0026(3)	.0108(3)	.0023(3)
C7	.4372(2)	.3270(1)	.3807(2)	.0268(4)	.0227(5)	.0212(4)	.0004(3)	.0102(3)	-.0021(3)
C10	.7241(2)	.3267(1)	.4641(2)	.0266(5)	.0297(5)	.0287(5)	-.0040(4)	.0023(4)	-.0019(4)
H1C5	.544(3)	.362(1)	.012(2)	2.7(3)					
H2C5	.269(3)	.361(2)	-.173(3)	3.1(3)					
HC6	.250(2)	.471(1)	.133(2)	2.1(2)					
HC7	.375(2)	.370(1)	.490(2)	2.8(3)					
H1C10	.802(3)	.367(2)	.609(3)	4.1(4)					
H2C10	.790(3)	.370(2)	.361(3)	3.8(3)					
Compound III									
N1	.3344(2)	.7503(4)	.3766(2)	.0184(10)	.0253(13)	.0263(12)	-.0006(10)	.0118(9)	-.0024(11)
N2	.2666(2)	.7808(4)	.2583(2)	.0165(10)	.0280(13)	.0279(13)	-.0017(10)	.0070(9)	-.0008(11)
C3	.3599(2)	.7982(5)	.1614(2)	.0156(12)	.0350(18)	.0171(12)	-.0035(12)	.0024(9)	.0014(12)
C4	.4751(3)	.6236(4)	.1631(3)	.0282(16)	.0246(16)	.0237(15)	-.0060(13)	.0124(11)	-.0026(13)
C5	.5582(3)	.5858(5)	.3083(3)	.0249(16)	.0214(15)	.0263(15)	.0051(12)	.0158(12)	.0007(12)
C6	.4964(2)	.7374(5)	.4001(2)	.0180(11)	.0249(15)	.0158(11)	.0026(12)	.0059(9)	.0003(11)
C7	.5757(3)	.9139(5)	.3414(2)	.0154(13)	.0277(15)	.0171(13)	-.0010(12)	.0032(10)	-.0014(12)
C8	.4919(3)	.9516(4)	.1956(2)	.0142(14)	.0217(15)	.0235(14)	-.0004(11)	.0062(10)	.0013(11)
C9	.5925(3)	.7882(5)	.1466(2)	.9194(12)	.0290(17)	.0157(13)	-.0021(12)	.0077(10)	-.0007(11)
C10	.6771(2)	.7513(5)	.2934(2)	.0156(11)	.0281(16)	.0200(12)	.0017(13)	.0066(9)	0012(13)
HC3	.298(3)	.823(5)	.074(3)	2.3(7)					
HC4	.446(3)	.509(5)	.104(3)	2.8(7)					
HC5	.580(3)	.445(5)	.338(3)	2.4(7)					
HC6	.533(3)	.703(4)	.494(3)	1.3(6)					
HC7	.611(3)	1.031(5)	.395(3)	1.9(7)					
HC8	.476(3)	1.097(4)	.167(3)	1.4(6)					
HC9	.632(3)	.809(4)	.069(3)	2.1(6)					
HC10	.783(3)	.739(5)	.332(3)	2.6(6)					

Table 2. Molecular dimensions with estimated standard deviations. The numbering of the atoms may be found in Fig. 1.

	Bond length (Å)	Corrected bond length (Å)		Bond angle (°)
Compound I				
N1−N2	1.255(4)	1.260	N2−N1−C6	114.7(1)
N1−C6	1.482(3)	1.487	N1−C6−C5	108.5(2)
C6−C5	1.537(3)	1.542	N1−C6−C7	106.8(2)
C5−C4	1.527(3)	1.533	C5−C6−C7	109.9(2)
C6−C7	1.535(3)	1.539	C6−C5−C4	108.5(2)
			C6−C7−C8	108.1(2)

C−H is in the range: 0.95−1.04 Å.

	Bond length (Å)	Corrected bond length (Å)		Bond angle (°)
Compound II				
N1−N2	1.255(2)	1.259	N2−N1−C6	114.9(1)
N1−C6	1.493(1)	1.497	N1−C6−C5	106.9(1)
C6−C5	1.534(2)	1.540	N1−C6−C7	105.4(1)
C6−C7	1.532(2)	1.538	C5−C6−C7	112.7(1)
C5−C4	1.532(3)	1.537	C6−C5−C4	108.6(1)
C7−C8	1.547(2)	1.553	C6−C7−C8	108.4(1)
C7−C10	1.552(2)	1.556	C6−C7−C10	119.2(1)
C10−C9	1.540(3)	1.545	C7−C10−C9	90.1(1)
			C8−C7−C10	89.9(1)

C−H is in the range: 0.97−1.02 Å.

	Bond length (Å)	Corrected bond length (Å)		Bond angle (°)
Compound III				
N1−N2	1.246(4)	1.251	N1−N2−C3	115.4(2)
N1−C6	1.464(4)	1.468	N2−N1−C6	115.9(2)
N2−C3	1.461(4)	1.464	N2−C3−C4	116.8(3)
C3−C8	1.544(4)	1.549	N2−C3−C8	117.0(3)
C3−C4	1.542(5)	1.548	C4−C3−C8	87.2(2)
C6−C7	1.543(5)	1.547	N1−C6−C5	116.2(3)
C6−C5	1.550(4)	1.555	N1−C6−C7	117.0(3)
C4−C5	1.530(5)	1.536	C5−C6−C7	87.0(2)
C4−C9	1.550(5)	1.554	C3−C4−C5	108.5(2)
C5−C10	1.560(5)	1.564	C3−C4−C9	90.3(2)
C7−C8	1.537(5)	1.543	C5−C4−C9	90.3(2)
C7−C10	1.555(5)	1.560	C6−C5−C4	108.6(3)
C8−C9	1.558(5)	1.563	C6−C5−C10	90.0(2)
C9−C10	1.546(4)	1.553	C4−C5−C10	90.3(2)
			C6−C7−C8	108.4(2)
			C6−C7−C10	90.4(2)
			C8−C7−C10	90.3(2)
			C3−C8−C7	108.5(2)
			C3−C8−C9	89.9(2)
			C7−C8−C9	90.1(2)
			C4−C9−C8	86.4(2)
			C4−C9−C10	90.1(2)
			C8−C9−C10	89.8(2)
			C5−C10−C7	86.2(2)
			C5−C10−C9	89.3(2)
			C7−C10−C9	89.9(2)

C−H is in the range: 0.94−0.98 Å.

Table 2. Continued.

Dihedral angles (°). The angles are positive in a righthand screw.

Compound I

C6−N1−N2−C3	1.5(4)	N2−N1−C6−C5	− 59.3(3)
N2−N1−C6−C7	59.2(3)	N1−C6−C5−C7	51.5(2)
C7−C6−C5−C4	− 65.0(2)	N1−C6−C7−C8	− 59.2(2)
C5−C6−C7−C8	58.4(2)	C6−C5−C4−C3	5.3(2)

Compound II

N2−N1−C6−C5	59.4(1)	N2−N1−C6−C7	− 60.8(1)
N1−C6−C5−C4	− 55.5(1)	C7−C6−C5−C4	59.9(1)
N1−C6−C7−C10	157.0(1)	N1−C6−C7−C8	56.5(1)
C5−C6−C7−C10	40.8(1)	C5−C6−C7−C8	− 59.8(1)
C6−C7−C10−C9	− 111.1(1)	C6−C7−C8−C9	120.8(1)

Compound III

C6−N1−N2−C3	0.2(4)		
N1−N2−C3−C8	− 50.6(4)	N1−N2−C3−C4	50.7(4)
N2−N1−C6−C7	50.1(4)	N2−N1−C6−C5	− 50.6(4)
N2−C3−C8−C9	137.5(3)	N2−C3−C8−C7	47.4(4)
N1−C6−C7−C10	− 136.9(2)	N1−C6−C7−C8	− 46.5(3)
N2−C3−C4−C9	− 137.8(3)	N2−C3−C4−C5	− 47.4(4)
N1−C6−C5−C10	137.6(3)	N1−C6−C5−C4	47.3(3)
C4−C3−C8−C7	− 71.4(3)	C4−C3−C8−C9	18.7(2)
C5−C6−C7−C8	71.4(3)	C5−C6−C7−C10	− 19.0(2)
C8−C3−C4−C5	71.6(3)	C8−C3−C4−C9	− 18.8(2)
C7−C6−C5−C4	− 71.4(3)	C7−C6−C5−C10	18.9(2)
C10−C9−C4−C3	108.5(2)	C8−C9−C4−C3	18.7(2)
C9−C10−C5−C6	108.7(2)	C7−C10−C5−C6	− 18.8(2)
C3−C8−C9−C10	108.7(2)	C6−C7−C10−C5	18.8(2)
C6−C7−C10−C9	108.2(2)	C3−C8−C9−C4	− 18.7(2)
C4−C9−C10−C7	− 86.2(2)	C8−C9−C10−C5	86.5(2)

dec-7-ene, $C_8H_{12}N_2$. Monoclinic, $a = 5.894(1)$ Å; $b = 10.038(3)$ Å; $c = 6.577(1)$ Å; $\beta = 113.83(2)°$; $(t = - 165 °C)$; $V = 365.0$ Å³; $M = 136.1$; $F(000) = 148$; $Z = 2$. $D_{calc} = 1.286$ g cm⁻³. Absent reflections: $(0k0)$ for k odd. Space group $P2_1/m$

Compound III. 7,8-Diazapentacyclo-[4.2.2.0².⁵.0³.⁹.0⁴.¹⁰]-dec-7-ene(diazabasketene), $C_8H_8N_2$. Monoclinic, $a = 9.249(2)$ Å; $b = 6.408(2)$ Å; $c = 10.294(2)$ Å; $\beta = 103.25(2)°$. $(t = - 165 °C)$; $V = 593.9$ Å³; $M = 132.1$; $F(000) = 280$; $Z = 4$. $D_{calc} = 1.477$ g cm⁻³. Absent reflections: $(h0l)$ for $h + l$ odd, $(0k0)$ for k odd. Space group $P2_1/n$.

STRUCTURE DETERMINATIONS

The structures were determined by the use of the program assembly MULTAN [25] and refined by Fourier and least-squares techniques. Anisotropic temperature factor parameters were introduced for nitrogen and carbon atoms; for hydrogen atoms positional parameters (cal-culated from stereo-chemical considerations) and isotropic thermal parameters were refined. In order to avoid the systematic errors in ΔF for the low angle data [17] the final least-squares refinement cycles included only observations with $\sin \theta/\lambda > 0.3$ with the refinement of only the nitrogen and carbon parameters.

The refinement converged to conventional R-factors of 0.046(I), 0.042(II) and 0.059(III) including all observed reflections. The corresponding weighted R-values were 0.038(I), 0.051(II) and 0.056(III). The standard deviations of an observation of unit weight, $[\sum w \Delta F^2 / (m-n)]^{\frac{1}{2}}$ were 1.58(I), 2.43(II) and 1.46(III) and the overdetermination ratios in the final refinements 10.0(I), 18.2(II) and 9.1(III).

Final atomic parameters are listed in Table 1. The experimental data may be obtained from the authors upon request.

A rigid-body analysis showed that the thermal motion of the molecules to a good approximation could be interpreted in terms of
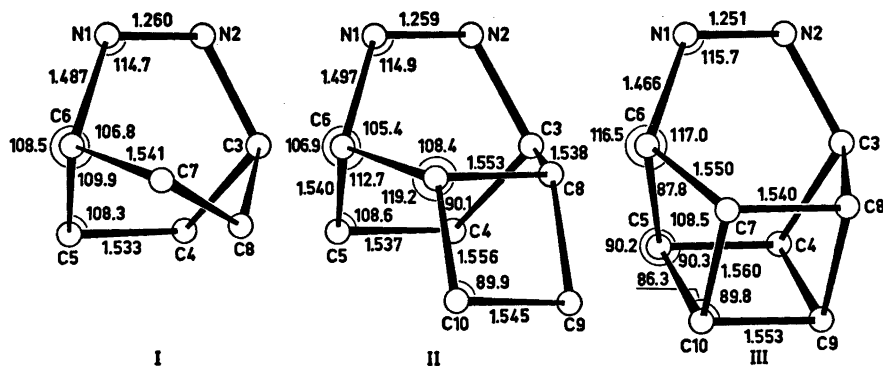
Fig. 1. Mean bond lengths and angles of chemically equivalent parameters. (In order to maintain the analogy between the compounds crystallographically equivalent atoms are given different numbers.

translational and librational oscillations (r.m.s.-ΔU were found equal to 0.0009 Å^2 (I); 0.0006 Å^2 (II) and 0.0012 Å^2 (III)). The bond lengths used during the discussion are those corrected for libration.[16]

Bond lengths and angles are listed in Table 2, dihedral angles involving the heavy atoms are also given. Estimated standard deviations are calculated from the variance-covariance matrix.

DESCRIPTIONS OF THE STRUCTURES

For all the three compounds the intermolecular forces in the crystals are of the van der Waals type. The shorter distances between molecules are mainly compatible with normal hydrogen-hydrogen contacts.

The molecular geometry may be seen from Fig. 1 where the atomic numbering is indicated. The bond lengths and angles given in the figure are mean values of those being chemically equivalent. Generally, when comparing distances and angles, differences of less than 0.01 Å and 0.5° may not be significant.

Compound I, 2,3-diazabicyclo[2.2.2]oct-2-ene. The molecular geometry is restricted by a crystallographic two-fold axis of symmetry passing between the nitrogen atoms and through the middle of the cyclohexane ring. The N−N double bond is 1.260 Å, the N−C bond 1.487 Å, and the C−C bonds are 1.542, 1.533 and 1.539 Å, respectively. The N=N−C angle is 114.7° which is very similar to the corresponding angle in aliphatic *trans*-azoalkanes (114.2−

116.0°)[7] but slightly larger than that found for aromatic *trans* species (113°).[9] The conformation of the cyclohexane ring is that of a skew boatform. The skewing, shown by the asymmetry in bond angles around C6 (Fig. 1) brings about a small deviation (5.3°) from an eclipsed conformation about the C4−C5 and C7−C8 bonds. The dihedral angle C6−N1−N2−C3 is 1.5°; the arrangement is thus nearly planar.

Compound II, 7,8-diazatricyclo[4.2.2.0^{2,5}]-dec-7-ene. This molecule exhibits mirror symmetry, the mirror plane being situated between the nitrogen atoms and normal to the N=N bond. The N=N bond length is 1.259 Å, the N−C bond 1.497 Å, and the N=N−C angle 114.9°. The C6−N1−N2−C3 arrangement is bound by the symmetry to be strictly planar and the geometry is nearly equal to that of Compound I. Except for the C7−C8 bond the C−C bonds of the cyclohexane ring are of the same length as those of Compound I, 1.538, 1.540 and 1.537 Å, respectively; the conformation is that of a pure boat form with planar C3−C4−C5−C6 and C3−C8−C7−C6 arrangements. By symmetry the cyclobutane ring is strictly planar, and with the possible exception of the C9−C10 bond the bond lengths are significantly longer (by 0.010−0.015 Å) than the normal aliphatic C−C bond. The conformations about all C−C bonds not involving C3 and C6 are eclipsed.

Compound III, 7,8-diazapentacyclo-[4.2.2.0^{2,5}.0^{3,9}.0^{4,10}]dec-7-ene (diazabasketene). The experimental values of bond lengths and

angles show that any deviation from *mm* symmetry for this molecule is insignificant. Our discussion is based on mean values given in Fig. 1 assuming this symmetry actually to be present.

The N=N bond is 1.251 Å, the C−N bond 1.466 Å and the angle C−N=N 115.9°. The C6−N1−N2−C3 arrangement is planar. The molecular fragment may be different from the corresponding part of the other two molecules, the C−N bond being significantly shorter, the C−N=N angle larger, and possibly, the N=N bond shorter. Excepting C7−C8 all C−C bonds, being members in fused cyclobutane rings, are longer than normal aliphatic C−C bonds. Two of the cyclobutane rings (C4−C5−C10−C9 and C7−C8−C9−C10) are planar with C−C−C angles close to 90°. The two remaining cyclobutane rings are equal and nonplanar. The angle between planes defined by C5−C6−C7 and by C5−C10−C7 (C4−C3−C8 and C4−C9−C8) is 153.7°. In the latter rings the bond angles are near 90° at C5 and C7 (C4 and C8) and 3−4° less at the other corners. The torsional angles are given in Table 2, the conformations about the bonds C4−C5, C7−C8 and C9−C10 are strictly eclipsed.

The geometry around the *cis*-azo moiety for I, II and III is very similar to that observed for two other *cis*-azoalkanes. An X-ray determination for a substituted pyrazoline [8] and a microwave study [19] of 2,3-diazabicyclo[2.2.1]-hept-2-ene yield C−N=1.50/1.52 and 1.506 Å, N=N=1.23 and 1.246 Å, ∠C−N=N=112/114 and 108.1°, respectively.

## DISCUSSION OF THE STRUCTURES

The influence of fused cyclobutane rings on the 2,3-diazabicyclo[2.2.2]oct-2-ene structure

Bond angles. As described above, I in the crystalline state has been found to possess a slightly twisted skeleton with C_2 symmetry. The most pronounced consequence of introducing a single four-membered ring (*i.e.* II) is to rigidify the [2.2.2]bicyclo system by reducing the bridge C−C dihedral angles to 0°. Concurrently the cyclobutane ring is required to be planar. Only three other pure organic substances bicyclo[2.1.0]pentane [20] (IV), the bas-

ketene photodimer [21] (V) and cubane [22] (VI), contain completely planar cyclobutane rings resulting from internal molecular forces alone. Except for a series of organometallic cyclobutane derivatives,[23] simple substituted cyclobutanes usually exhibit dihedral angles around 26°. Certain compounds with a crystallographic center of symmetry have planar four-membered rings presumably as a result of crystal packing forces.[23]

IV   V   VI
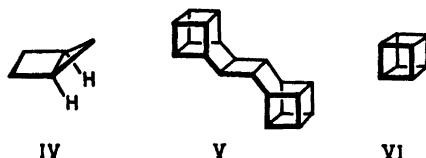
Angle distortion around the bridgehead carbons of II suggest the existence of H···H steric repulsion between the fused cyclobutane and the CH$_2$−CH$_2$ bridge. Thus the ∠CCC of 112.7° (II') has expanded by 2.8° as compared with the same angle of I. Accordingly the complimentary angles 105.4° and 106.9° (II') are compressed by 1.5−2.0°. The strain is likewise evidenced around the cyclobutane bridge with a ∠CCC of 119.2°. The corresponding angle for a cyclobutane fused to a non-bicyclic six-membered ring (*i.e.* a bicyclo[4.2.0]octane system) is 113±0.5°.[24] Finally the HCH angle of both the cyclobutane ring (108.9°) and the CH$_2$−CH$_2$ bridge (108.0°) is reduced relatively to cyclobutane [23] (110−114°) and I.
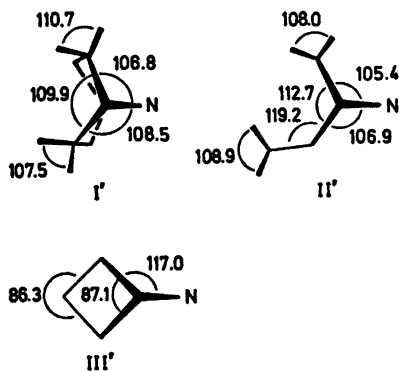
The formal act of bonding the cyclobutane ring of II to the CH$_2$−CH$_2$ bridge generates three new four-membered rings and leads to diazabasketene III. Two unique cyclobutane ribbons can be identified. The bicyclohexane

fragment bisected by the symmetry plane passing through the N=N bond contains two planar cyclobutane rings. The relative lengths of the three different C−C bonds involved in this unit are in the same relative order as those found for bicyclo[2.2.0]hexane [25] (VII). The bridge angle for III (86.3°), however, is considerably diminished relative to the 113.5° value for the latter. Each of the rings of VII exhibits a puckering angle (β) of 11.5°.

The second cyclobutane sequence in diazabasketene contains the rings bonded to nitrogen. The isolated three-ring fragment is depicted by structure VIII. The central cyclobutane is planar, whereas the flanking rings are both twisted outward with $\beta = 26.3°$. By contrast the cyclobutanes of *syn*-tricyclo[4.2.0.0^{2,5}]-octane [26] (IX) are all puckered ($\beta = 9.8°$) but in the same screw-sense. Consistent with the inclusion of IX in the condensed diazabasketene structure, the angle between adjacent ring carbons (108.5°) is considerably reduced relative to that in IX.

113.5°   108.0°   119.0°
VII   VIII   IX

Bond lengths. Two noteworthy changes in bond distances for the I−III series concern the C−N and N=N bonds. The latter is constant in the transition from I to II, but drops by about 0.01 Å from II to III. By contrast the C−N bond lengthens by 0.01 Å from I to II, then shrinks by 0.03 Å from II to III.

Although these variations are small, their direction is significant and entirely consistent with the results of a recent photoelectron (PES) study for I, II and III.[4,6] The lone pair (n_- and n_+) and π(NN) molecular orbitals have been assigned as shown in Fig. 2 by assuming the validity of Koopmans theorem.[27] Whereas the antisymmetric n_- MO rises only slightly in energy along the I−III series, π(NN) drops slightly and n_+ falls markedly. The pattern of the changes has been rationalized by considering both conformational differences and the effect of through-space interaction[28] between the N=N unit and the cyclobutane and bicyclobutane fragments, respectively.[4,6] Fig. 3 illustrates the situation for n_+ of diazabas-
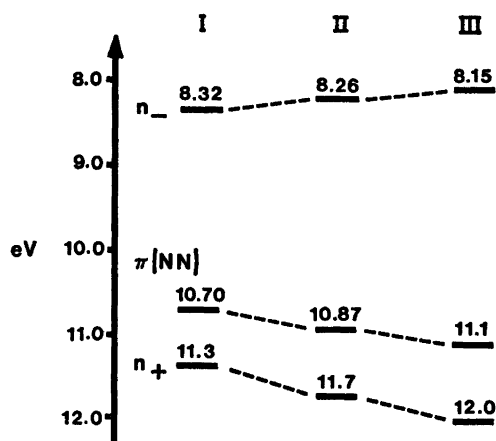
Fig. 2. Experimental ionization potentials (photoelectron spectroscopy) for the nitrogen lone pairs (n_- and n_+) and the π(NN) bonds of azoalkanes I, II and III. Refs. 4 and 6.

ketene and the highest occupied a_1 MO of bicyclohexane.[29] Interaction of the a_1 symmetry species leads to the stabilization of n_+ and the destabilization of $8-a_1$. Of necessity lower energy a_1, b_1 and b_2 orbitals of bicyclohexane combine with the corresponding MO's of the azobicycle leading to the final MO distribution in III. The detailed interaction diagram will be presented in a forthcoming report.

The implication of the PES results for III is obvious. The stepwise introduction of cyclobutane rings into the 2,3-diazabicyclo[2.2.2]oct-3-ene structure stabilizes the MO's associated with N−N bonding leading to a shorter N=N bond. Unfortunately the constancy of the same bond distance from I to II is not accomodated by this straightforward analysis. We have therefore performed CNDO calculations[30] for structures I−III in the hope of gaining additional insight. The MO energy trends implied by Fig. 2 are reproduced. For lower-lying MO's with the same symmetry as n_+ (b, c and d, Fig. 4), the calculations predict essentially no change or a moderate stabilization for analogous orbitals in I and II. In actuality, even if the low-lying MO energies were quantitatively evaluated by the calculation, the relative energies of nearly degenerate orbitals are only a very rough guide to the strength of the N−N and C−N bonding. All of the MO's in question are highly delocalized and contain non-trivial
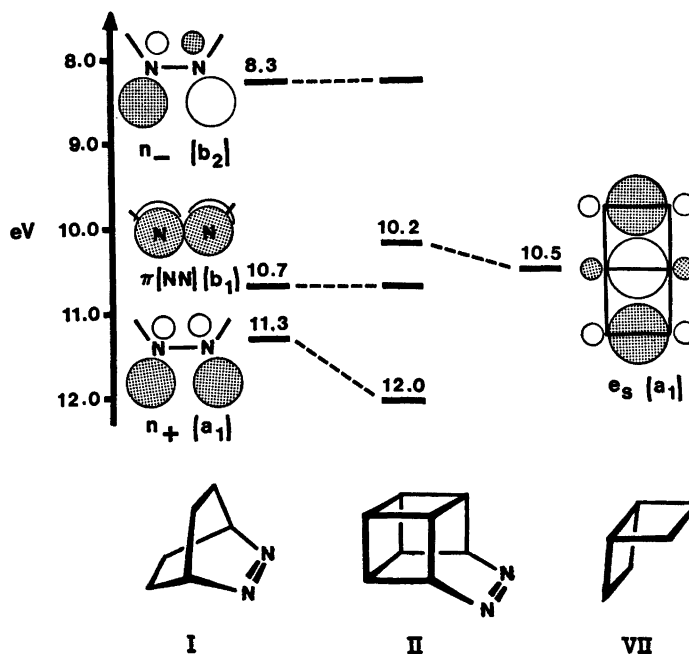
Fig. 3. Interaction of the a_1 molecular orbitals between azoalkane I and bicyclo[2.2.0]hexane leading to stabilization of n_+ in diazabasketene (III). Additional MO interactions not illustrated.

contributions from the carbon skeleton. By contrast the corresponding diazabasketene orbitals are calculated to be greatly stabilized relative to II (0.75 – 3.0 eV).

Of particular note is the prediction that low-lying N – N and C – N MO's for I and III are pure σ in composition, whereas certain of the corresponding energy levels for II contain considerable π-character (Fig. 4). This can be rationalized by noting that the cyclobutane plane makes a 120.8° angle with the plane of the CH – CH bridge to which it is fused. The orientation of the four-membered ring is such that it lies unsymmetrical with respect to the nodal plane of the hypothetically isolated π(NN) (*cf.* II'). In diazabasketene the two corresponding cyclobutane rings (*i.e.* the bicyclohexane moiety) are oriented symmetrically about this π-bond. Thus for II the appropriate cyclobutane MO (*i.e.* the e_s MO [31]) interacts through-space with the – CNNC – fragment leading to orbitals with mixed $\sigma - \pi$ character (*e.g.* – 12.7, – 13.0 and – 13.8, b and c, Fig. 4). The latter is, no doubt, partly responsible for the similar energies of comparable low-lying

MO's of I and II. More to the point, analogous orbitals with significant N – N bonding properties are expected to contribute less to the N – N bond energy the greater the degree of π-mixing. Thus we postulate that relative to I, the stabilization of π(NN) and n_+ is offset by the weaker π-bonding of the lower energy orbitals in II. The net effect is to leave the N = N distance unchanged in I and II.

Variations in the C – N bond lengths are described by a similar analysis. The characteristic MO's are shown in Fig. 4. The orbital containing the greatest C – N contribution is n_-, experimentally and theoretically higher in energy in II than in I. Lower-lying MO's for the former, as is the case for the N – N link, contain considerable π-type bonding. On this basis the C – N bond in II is expected to be weaker and therefore longer than in I as is observed.

The transition to diazabasketene reverses the trend. Although its n_- lies highest in the I – III series, III's low-lying C – N MO's are completely σ in character and significantly lower in energy than the corresponding energy levels

I   II   III

a.

−10.1   −9.8   −9.5

b.

−12.7   −12.7   −15.7

−13.0

c.

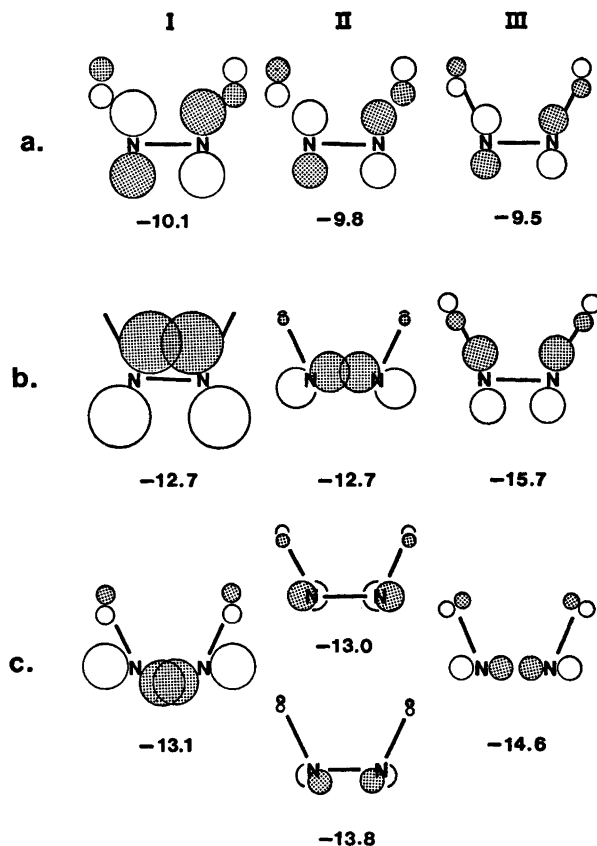−13.1   −14.6

−13.8

Fig. 4. Partial CNDO[30] eigenfunctions for certain N−N and N−C centered MO's of I, II and III. Only the nitrogen bridge and bridgehead carbon contributions are shown. Circle radii represent the squares of the relative atomic orbital compounds among the orbitals pictured. The numerical value associated with each MO is the CNDO predicted energy in eV.

for I and II. Accordingly the C−N bonds in diazabasketene are stronger and shorter by comparison.

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