Photoelectron Spectra of Diazabasketene, Diazadeltacyclene,[1] and Related Polycyclic *cis*-Azoalkanes

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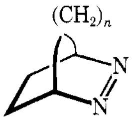
Abstract: The He(I) photoelectron spectra of diazabasketene (**2**), the cyclobutanated [2.2.2] system **3**, and diazadeltacyclene (**5**) are reported. For all three substances level assignments lead to the MO sequence: $n_- > \pi > n_+$. In order to assist with the assignment of diazabasketene, the PE spectrum of basketene has been measured. Unlike the situation for simple *cis*-azo bicyclics, high-lying σ orbitals associated with the cyclopropane and cyclobutane moieties fall between n_- and π(NN). The orbital interactions responsible are simultaneously the cause for a n_-/n_+ splitting of about 3.8 eV for diazabasketene and 4.0 eV for diazadeltacyclene. These values are the largest so far observed for *cis*-azoalkanes. The importance of ground-state homoconjugation for multicyclic azo compounds containing three- and four-membered rings is discussed in terms of molecular conformation and nitrogen extrusion rates. Caution is urged in the application of PES determined MO sequences to the relative energy of the corresponding transition states for retrocycloaddition reactions involving nitrogen. The partial determination of structural parameters for the title compounds and complete determination for some related bicyclics by MO calculations are discussed. And finally a problem associated with the interpretation of the PE spectra of large molecules is described.

The study of the electronic structure of organic molecules and the rationalization of the pathways of chemical reactions have been given new impetus recently by the work of Fukui,[3a] Hoffmann,[3b] Pearson,[3c] and others[4] on orbital interactions. These interactions are either intermolecular or intramolecular in nature. The former provide the basis for various sets[3,5] of symmetry rules for chemical reactions which have been applied with considerable success to a large variety of systems. Intramolecular interactions are especially interesting in molecules which have two or more localized, or semilocalized, orbitals of the π bonding and lone pair types. These localized orbitals, or groups of localized orbitals, may interact either directly or indirectly with each other. The relative importance of these two modes of interaction, known as through-space and through-bond interaction, respectively, can only be evaluated by means of molecular orbital (MO) calculations whereas the magnitude of the splitting associated with the interaction of two localized orbitals can be investigated experimentally by photoelectron spectroscopy (PES).

In this paper we are concerned with the interaction of lone pair orbitals on adjacent nitrogen atoms and their further interaction with various three- and four-membered ring carbon units in a multicyclic molecular frame. PES has been used to determine the splitting between the symmetric combination of lone pair orbitals n_+ and the antisymmetric combination n_- in diimide,[6] *trans*-azomethane,[7] diazirine,[8] several aliphatic cyclic and multicyclic *cis*- and *trans*-azo molecules,[9-11] and hydrazines.[12,13] As a sequel to our earlier study[10] of the 2,3-diazabicyclo[2.2.*n*]alk-2-enes (*n* = 1, 2, 3, 4) **1**(*n*), we report here the PE spectra of diazabasketene (**2**) and diazadeltacyclene (**5**). In order to help in the assignment of the π bands, the PES of basketene (**7**) and 7,8-diazatricyclo[4.2.2.0^{2,5}]dec-7-ene (**3**) have been measured. We also rediscuss the assignment of **1**(*n*) in view of the additional results presented in this paper.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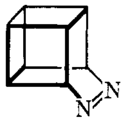
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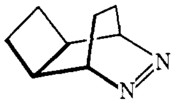
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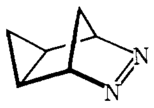
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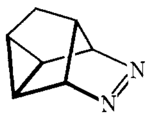
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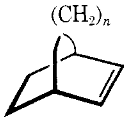
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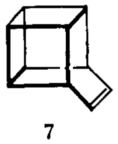
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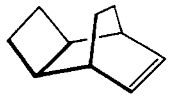
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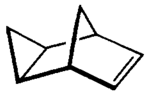
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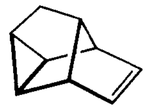
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The title compounds **2** and **5** are related to **1**(2) and **1**(1), respectively, through the addition of the appropriate bridging groups in the sense that the azo functional group is contained within two six-membered rings in **1**(2) and **2** and within one five-membered and one six-membered ring in **1**(1) and **5**. In terms of a semilocalized picture of the electronic structure of *cis*-azo molecules, the addition of bridging groups to **1**(1) and **1**(2) introduces new molecular orbitals which interact, provided they have the correct symmetry, with the high-lying n_- lone pair orbital centered on the nitrogen atoms. This additional delocalization leads to a destabilization of the n_- lone pair orbital and a corresponding decrease in the first ionization potential (IP). This simple picture is in complete agreement with the PE spectra and semiempirical MO calculations discussed below. To assign the other bands in the PE spectra of **2** and **5** it is not sufficient to look for similar systematic changes in the spectra of **1**(1) and **1**(2), respectively, but rather it is necessary to appeal to the results of MO calculations and empirical correlations with related molecules.

Experimental Section

Melting points were taken on a Gallenkamp apparatus and are uncorrected. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 257; proton NMR, Varian A60-A; He I photoelectron spectra of **2** and **5** were taken on a pre-

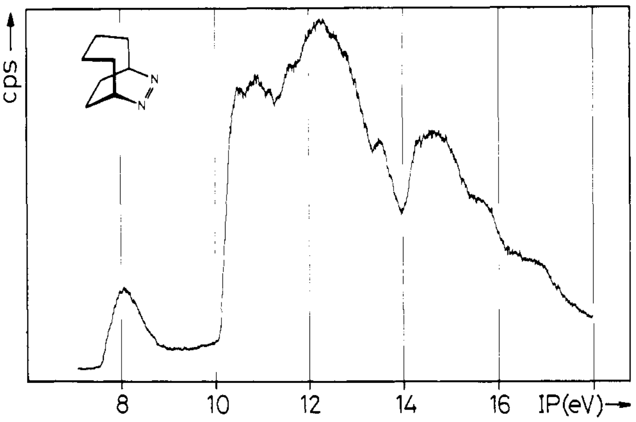


Figure 1. Photoelectron spectrum of **1**(4).

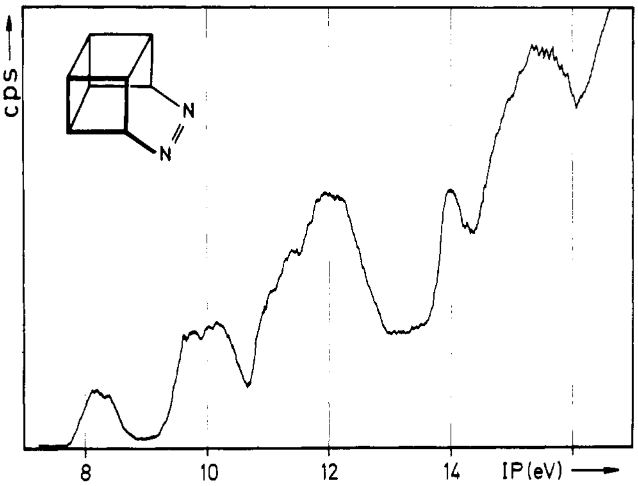


Figure 2. Photoelectron spectrum of diazabasketene (**2**).

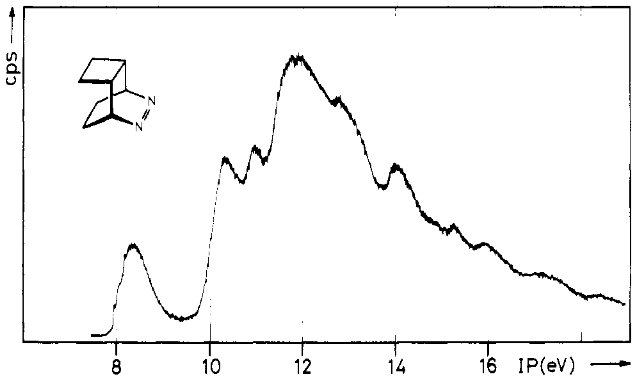


Figure 3. Photoelectron spectrum of cyclobutyl azo compound **3**.

viously described spectrometer[14] and calibrated with xenon as internal standard.[15] Conventional sample handling was used for **5**, but for **2** it was necessary to use a direct inlet system due to low volatility. A PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England) was used to record the spectra of **3** and **7** and to reinvestigate **1**(3) and **1**(4). The new IP's agree to within 0.03 eV with the values determined by use of the other spectrometer.[14] Because a better signal-to-noise ratio was achieved for **1**(4), four IP's could be resolved in the 10.5 to 12 eV region which was not the case in our previous study.[10] For that reason we report the spectrum of **1**(4) in Figure 1.

The photoelectron spectra of **2**, **3**, **7**, and **5** are reproduced in Figure 2, 3, 4, and 5, respectively. It should be mentioned that the PS-18 spectrometer is operated by scanning the potential difference between the electrodes of the analyzer; this implies a discrimination against low kinetic energy electrons and as a result the PE spectra of **1**(4), **3** and **7** display a falling off of intensity at high IP.

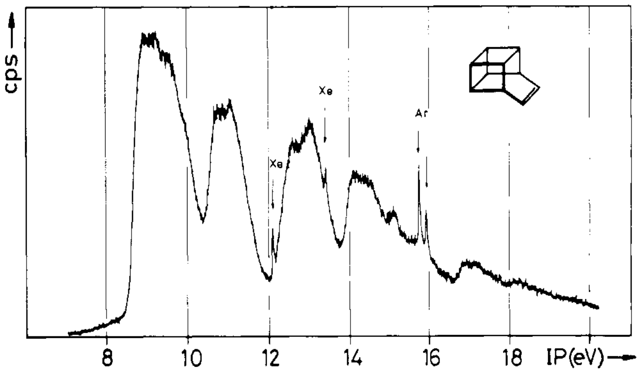


Figure 4. Photoelectron spectrum of basketene (**7**).

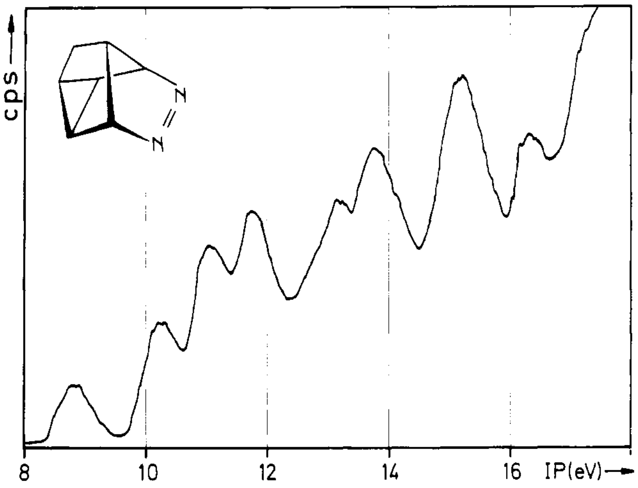


Figure 5. Photoelectron spectrum of diazadeltacyclene (**5**).

This effect is not observed in the spectra of **2** and **5** because of the different scanning mode (retarding field) of the spectrometer[14] used to record the spectra. The observed vertical IP's are compiled in Table I.

Combustion analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

7,8-Diazapentacyclo[4.2.2.0^{2,5}.0^{3,9}.0^{4,10}]dec-7-ene (Diazabasketene) (2). (a) 4-Phenyl-2,4,6-triazatetracyclo[5.4.2.0^{2,6}.0^{8,11}]-9,12-tridecadiene-3,5-dione (11). Prepared as described for the corresponding *N*-methyl adduct[16] by treatment of the precursor dibromide (50.0 g, 1.14 mmol, mp 253.5-257.5 °C dec) with zinc-copper couple. The resulting sparkling white solid (27.2 g, 0.975 mmol, 86%) was spectroscopically identical (ir) with the analytical sample: mp (CCl_4) 216-217 °C; ir (KBr) 1775 (m), 1712 (s), 1408 (s), 855 (m), and 784 cm^{-1} (s); NMR, τ($CDCl_3$/TMS) 2.59 (5 H, s with baseline broadening), 3.80 (3 H, t), 3.99 (2 H, s), 4.95 (2 H, q), 6.65 (2 H, d).

Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.13; H, 4.77; N, 15.06.

(b) Photolysis of Phenylurazolediene (11). 4-Phenyl-2,4,6-triazahexacyclo[5.4.2.0^{2,6}.0^{8,11}.0^{9,13}.0^{10,12}]tridecane-3,5-dione (12). Dione **11** (10.0 g, 35.8 mmol) was dissolved in acetone (1000 ml). The clear solution, stirred magnetically, was irradiated with a Hanovia 200 W high-pressure mercury vapor lamp. The uv source resided in a water-cooled quartz immersion cell employed in conjunction with a vycor filter (radiation of greater than 2400 Å passed). After 29 h the acetone was removed in vacuo. The relatively clean solid was washed with absolute ethanol (8.4 g, 84.0%). It had an infrared spectrum identical with that of an analytical sample. Double crystallization from the same solvent resulted in white rods: mp 193-194 °C; ir (KBr) 1757 (s), 1701 (s), 1404 (s), 762 (s), 690 cm^{-1} (s); NMR τ($CDCl_3$/TMS) 2.55 (5 H, m), 4.92 (2 H septet), 6.32 (4 H, quintet), 6.80 (2 H, quintet).

Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.13; H, 4.73; N, 15.06.

Table I. Vertical Ionization Potentials (IP's, eV)[a] of **1**, **2**, **3**, **5**, and **7**

Band	**1**(1)	**1**(2)	**1**(3)	**1**(4)	**2**	**3**	**5**	**7**
1[b]	8.96	8.32	8.15	8.05	8.15	8.26	8.83	8.97
2	11.53	10.70	10.56	10.51	9.73	10.25	10.25	9.18
3	11.91	*c*	11.4	10.86	10.16	10.87	11.06	9.50
4	12.7[e]	11.45	12.0[e]	11.12	11.1[e]	11.7[d]	11.73	9.8[e]
5	13.2[d]	12.7	12.5[e]	11.6[e]	11.4[e]	12.7[d]	12.8[e]	10.80
6	14.0	13.9[d]	13.1	12.2[d]	12.0[d]	13.9	13.1[e]	11.06
7	15.8	16.0[d]	14.4[d]	13.5	13.98	14.6	13.8	12.7
8	16.7[e]	16.9[d]	15.4	14.6[d]	14.9[e]	15.1	15.2[d]	13.0
9	17.5		16.4[e]	15.8[e]	15.5[d]	15.8	16.2	14.2
10			16.8	16.8		17.0		14.5[f]

[a] Vertical IP's are taken as the maxima of the Franck–Condon envelopes; ±0.05 or ±0.1 eV. [b] Adiabatic IP's (onset of band) are: 8.45, 7.79, 7.60, 7.37, 7.68, 7.68, 8.23, and 8.34 ± 0.05 eV, respectively. [c] Complex band with two maxima at 11.20 and 11.37 eV. [d] Maximum of a broad band which certainly contains more than one ionization. [e] Shoulder. [f] Plus additional vertical IP's at 15.1, 15.6, 17.0, and 18.2 eV.

(c) **Diazabasketene (2).**[17] A nitrogen stream was bubbled for 10 min into a slurry of cage-compound **12** (7.65 g, 27.4 mmol) in ethylene glycol (65 ml). Distilled water (65 ml) containing potassium hydroxide (11 g, large excess) was mixed with the glycol slurry as the nitrogen purging was continued for 10 min. A few boiling stones were introduced and the flask was fitted with a simple still head with a nitrogen inlet. The flask, its contents under a nitrogen blanket, was heated strongly over a wire gauze and a burner flame. As the initial solid went into solution a much bulkier gelatinous-like solid appeared (partially hydrolyzed **12**). Continued heating for a total of 10 min urged this material into solution as a deep red distillate (56 ml) was collected. Distilled water (50 ml) was added quickly to the clear reaction solution causing an immediate heavy precipitate. Heating was resumed for 10 min as further deep pink distillate was collected (50 ml). Again distilled water (50 ml) was added to the clear yellow solution affecting a transient cloudiness. Heat was applied for a final 5 min accompanied by collection of more distillate (25 ml). The cooled clear butterscotch colored residual solution was diluted to three times its volume with water (a clear solution resulted) and extracted ten times with methylene chloride (1000 ml). The combined extracts were dried over sodium sulfate (coloring from yellow to deep red on standing; it is best not to allow the extracts to stand longer than 2 h) and stripped of solvent in vacuo. The residual dark brown oil was extracted many times with warm hexane (in most cases until the hydrocarbon no longer comes away from the oil cloudy). This petroleum ether solution was allowed to stand at room temperature for 30 to 60 min while suspended brown oily material settled to the bottom of the beaker. The clean yellow-green supernatant was decanted in portions into a second beaker, warmed briefly to boiling on a hot plate, treated with a bit of activated charcoal, and filtered hot (the fritted glass funnel was prewarmed). As the solvent was evaporated under aspirator pressure a pale yellow-green solid precipitated. This was filtered and air dried when all but a small portion of hexane had been removed (2.10 g, 58%). An infrared spectrum of this material is almost identical with that of an analytical sample save for a weak band at 1890 cm^{-1}. Triple low-temperature crystallization from 30-60 °C petroleum ether produced white needles which decomposed at 109-111 °C (sintered from 100 °C). Similar purity was achieved by room-temperature sublimation at 0.05 mm of pressure: ir (CH_2Cl_2) 3012 (s), 1517 (m), 1495 (w), 1163 (s), 1076 (m), 961 cm^{-1} (m); uv $\lambda_{\max}$ (isooctane) 373 (sh, log ϵ 1.94), 381 (sh, 2.20), 387 (2.37), 390 (2.51), 394 (2.38), 403 (2.68), 412 nm (sh, 1.43); nmr τ ($CDCl_3$/TMS) 3.73 (2 H, septet), 6.70 (2 H, quintet), 7.45 (4 H, m).

Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.44; H, 6.10; N, 20.97.

Throughout the above described manipulations, the volatile azo substance discolors the skin, filter paper, soapstone desk top, etc., a crimson or purple. An analogous coloration appears when diazabasketene **2** is treated with acid.

6,7-Diazatetracyclo[3.2.1.1^{3,8}.0^{2,4}]non-6-ene (Diazadeltacyclene) (5). Prepared by the semicarbazide-copper halide method[18]; mp 102-103 °C (lit.[19] 95-97 °C).

7,8-Diazatricyclo[4.2.2.0^{2,5}]dec-7-ene (Cyclobutylazoalkene) (3). The azo-*N*-oxide of **3**[16] (1.37 g, 9.0 mmol) in $CHCl_3$ (25 ml) was treated with an excess of hexachlorodisilane[20,21] at room temperature until the oxide was no longer detectable by TLC. The reaction mixture was treated with water (20 ml), basicified with aqueous NaOH, extracted with $CHCl_3$, and dried ($MgSO_4$). Solvent evaporation led to a white crystalline solid with an NMR identical with that of an analytical sample (0.682 g, 5.0 mmol). The material was sublimed, recrystallized (pentane), and resublimed several times: mp 142-144 °C (lit.[22] 142-143 °C); nmr τ ($CDCl_3$-TMS) 5.07 (2 H, broad s), 7.93 (8 H, m), 8.85 (2 H, m).

Assignment of the Diazabasketene PE Spectrum

As in the case of the bicyclic *cis*-azo molecules[10] **1**(*n*) we assign the relatively broad band for the first IP of diazabasketene to the ionization of the antisymmetric combination of lone pair orbitals n_-. This assignment is supported by analogy with other molecules containing lone pairs on adjacent nitrogen atoms and the results of MO calculations.

Comparison of several multicyclic alkenes[23] with their diaza analogues[9a,10] indicates that the IP for the removal of an electron from a π(NN) orbital is usually ca. 1.6 to 2.6 eV higher than the IP of the corresponding π(CC) orbital, the upper values corresponding to more strained molecules. If this empirical observation is general and if the first IP (Table I) of basketene is assigned to the π orbital, then the π band of **2** would be expected in the region of 10.6 to 11.6 eV. On this basis one of the shoulders observed at 11.1 and 11.4 eV would be expected to correspond to ionization of the π orbital of diazabasketene. This in turn implies that at least one of the second and third bands arises from the removal of an electron from high-lying σ orbitals. Evidently the first IP of basketane has not been reported but it is known that cubane has a very low (8.74 eV) first IP[23a] and, therefore, it is not unreasonable to expect σ bands at low ionization energies in diazabasketene.

To assist with the assignment of the PE spectrum of diazabasketene we now consider the results of CNDO calculations with two dissimilar sets of parameters[24,25] and an INDO[26] calculation. The data obtained from one set of parameters[25] for **1**(1), **1**(2), **2**, **3**, and **5** are listed in Table II. It should be stressed that these results represent the MO scheme for one of the many calculations we have carried out and that changes in the parameters, the method, or the geometries can alter the order of the levels because of the small differences between many of the molecular orbitals. In a later section of this paper we discuss the geometries for our calculations but in this section we are primarily concerned with the ordering and symmetries of the MO's. Application of Koopmans' theorem to the results of the three MO calculations suggests that the first band arises from the removal of an electron from a b_2 orbital (assuming C_{2v} symmetry for **2**), namely the n_- lone pair orbital, and that the second and third bands arise from the ionization of a_2 and a_1 MO's. The latter two have very little electron density on the nitrogen atoms and can be classified as the e_a and e_s orbitals, respectively, arising from the bicyclo[2.2.0]hexane fragment of **2**.[27] Both CNDO calculations predict the fourth band to be a b_1 orbital which is the π orbital, where-

Table II. Orbital Energies[a] (eV) and Symmetries[b,c] of **1**(1), **1**(2), **2**, **3**, and **5**

1(1)	**1**(2)	**2**	**3**	**5**
-10.39 a$''$(n$_-$)	-9.94 b$_2$(n$_-$)	-9.05 b$_2$(n$_-$)	-9.81 a$''$(n$_-$)	-10.11 a$''$(n$_-$)
-10.91 a$'$(π)	-10.71 a$_1$(σ)	-9.53 a$_2$(e$_a$)	-10.15 a$'$(e$_s$)	-10.39 a$'$(π)
-11.38 a$'$(n$_+$)	-10.88 a$_2$(σ)	-10.28 a$_1$(e$_s$)	-10.51 a$''$(σ)	-10.73 a$'$(e$_s$)
-11.43 a$''$	-11.21 b$_1$(π)	-10.68 b$_1$(π)	-11.03 a$'$(π)	-11.12 a$''$(e$_a$)
-11.85 a$''$	-12.34 a$_2$	-11.10 a$_2$	-11.42 a$''$(e$_a$)	-11.28 a$''$(n$_+$)
-12.44 a$'$	-12.35 b$_2$	-11.27 b$_2$	-11.62 a$'$(n$_+$)	-11.45 a$'$
-12.62 a$'$	-12.58 a$_1$(n$_+$)	-11.35 a$_1$	-11.95 a$''$	-11.72 a$''$
-12.74 a$''$	-12.61 b$_1$	-11.98 a$_1$(n$_+$)	-12.33 a$'$	-11.89 a$'$

[a] Computed in the CNDO approximation with the parameters of ref 25 and the geometries shown in Figure 9. [b] C_s point group for **1**(1), **3** and **5** and C_{2v} point group for **1**(2) and **2** with the y axis coincident with the N═N bond and the z axis coincident with the C_2 symmetry axis. [c] Undesignated orbitals are σ.

as the INDO calculation places it as the fifth band. The CNDO calculations yield the third highest a$_1$ MO as the eighth band; the INDO scheme lists it seventh. For reasons given in the last section, this MO is designated as the n$_+$ lone electron pair (cf. Figure 10). In agreement with previous studies of *cis*-azo molecules the calculations predict the order for the lone pair and π orbitals of **2** to be: IP(n$_-$) < IP(π) < IP(n$_+$).

In view of the above considerations we assign the first four bands in the PE spectrum of diazabasketene as follows: 8.15 (b$_2$, n$_-$), 9.73 (a$_2$, σ(e$_a$)), 10.16 (a$_1$, σ(e$_s$)), and 11.1 (b$_1$, π). The 11.4 eV IP surely belongs to one of the intervening σ orbitals b$_2$, a$_1$, or a$_2$. The multiple ionization peak at 12.0 eV is assigned to the remaining two, the a$_1$(n$_+$), and may contain others as well. Other IP's are σ in character.

Thus we conclude that the n$_-$/n$_+$ splitting of approximately 3.8 eV in **2** is somewhat larger than the interaction observed for three- and five-membered ring *cis*-azo molecules[8,9] and considerably greater than the splitting observed for four-membered rings.[9a] The magnitude of Δn is mainly due to the interaction of n$_-$ and n$_+$ with the e$_a$ and e$_s$ MO's, respectively, of the rigidly and favorably oriented bicyclohexane unit. A population analysis of the CNDO eigenvectors for both n$_-$ and n$_+$ confirms the mixing. A similar efficient interaction of bicyclohexane and π(CC) MO's has been observed for hypostrophene.[28] The above interpretation likewise finds support in the low n$_-$ IP value and in the uv spectrum of **2**; the n $\rightarrow$ π^* transition ($\lambda_{\max}$ (isooctane) = 403 nm, ϵ = 480 M^{-1} cm^{-1}) falls at the longest wavelength observed so far for a *cis*-azo compound, implying that n$_-$ is considerably destabilized.

The lone-pair splitting (Δn) of simple azo molecules has been discussed as a function of the NNC angle by other authors using different MO treatments. Brogli et al.[9a] recently tried to rationalize the PES-Δn values of complex molecules by proposing a quantitative, empirical relationship between Δn and the NNC angle. The latter adequately describes the situation for **2**, but fails for **1**(2) where the predicted splitting is 0.7 to 0.9 eV too large. For an NNC angle of 115° (cf. molecular geometry section) the calculated splitting is 3.8 eV, while the observed one is 2.9 or 3.1 eV (cf. Table I). Consequently it is clear that such rationalizations take into account only one aspect of a much more complex interaction diagram, and that they should be used only for series of compounds for which other relevant orbital interactions are known to be of minor or constant importance.

The Cyclobutyl Derivative 3

In an attempt to correlate the PE spectra of **1**(2) and **2** and to gain possible insight into the influence of cyclobutane substitution on the energies of the π and n$_+$ orbitals, we have recorded the spectrum of tricycle **3**.

The first IP is assigned to the removal of an electron from the n$_-$ lone pair orbital for the same reason given in the case of **2**. Again the calculations[25] (cf. Table II) suggest that the next two IP's arise from MO's associated with the hydrocarbon part of the molecule (a$'$ and a$''$). For the higher-lying a$'$ MO, the largest coefficients are observed for the atomic orbitals centered on the four carbon atoms of the four-membered ring. The fifth MO (a$''$) may be described similarly. These are the e$_s$ and e$_a$ MO's, respectively, of the cyclobutyl fragment where the subscripts denote the splitting of the doubly degenerate e$_u$ MO of cyclobutane[27] (D_{2d} symmetry) into symmetric and antisymmetric combinations with respect to the C_s mirror plane applicable to **3**. The lifting of the degeneracy is, of course, a consequence of the reduction in symmetry which accompanies the fusion of the cyclobutyl moiety to an azo fragment to give **3**.

The third energy level, a$''$, is described by the calculation to be a framework MO located almost exclusively on the carbon six-membered ring. The fourth highest occupied MO has a$'$ symmetry and is clearly identified as the π(NN) MO. The fifth (e$_a$) and sixth MO's are close in energy with the latter one being identified as the n$_+$ lone pair. Exactly the same order is obtained with CNDO/2 which yields -11.07, -12.42, -13.36, -13.96, -15.26, and -15.33 eV for the orbital energies of the highest occupied MO's. In this case the fifth and sixth levels are even closer in energy.

The assignment of the PE spectrum of **3** is complicated by the fact that the fourth as well as the fifth bands appear to arise from more than one ionization. Thus although it is quite probable that the first IP should be assigned to the n$_-$ lone pair and the second to e$_s$, the disposition of π(NN) and n$_+$ is less certain. For the former we resort to the experimental correlation between π(CC) and π(NN) ($\Delta E(\pi)$ = 1.6–2.6 eV). The π IP for hydrocarbon **8** is found at 9.0 eV.[23c] The differences between this value and the third and fourth ionizations of **3** are 1.9 and 2.7 eV, respectively. According to the $\Delta E(\pi)$ criterion both ionizations could thus arise from a π orbital. However, for the bicyclo [2.2.2] skeleton (i.e. **1**(2), Table I, and **6**(2)[23c]), $\Delta E(\pi)$ = 1.7 eV. Thus we assign the 10.87 eV ionization to the π MO, implying that a structural supplementation of **1**(2) to give the cyclobutane derivative **3** leads to a stabilization of π(NN) by 0.17 eV. The latter would amount to ca. 1 eV, if the π orbital were found at 11.7 eV instead. Further support for our assignment is provided by the fact that for a number of bicyclic [2.2.1] and [2.2.2] systems, anti-fused cyclopropyl rings stabilize π(CC) and π(NN) a maximum of 0.35 eV.[23c,29,30] A similarly substituted cyclobutyl unit usually influences the π orbital less than the corresponding three-membered ring, although a value as high as 0.25 eV has been recorded.[30]

A consequence of this interpretation is that e$_s$ and π(NN) lie within 0.5 eV of one another and might best be described as arising from a nontrivial interaction. Ionization from such a mixed (e$_s$ + π) orbital could account for the lack of fine structure in the π IP.

The prediction that a σ(CC) (a$''$) lies between e$_s$ and

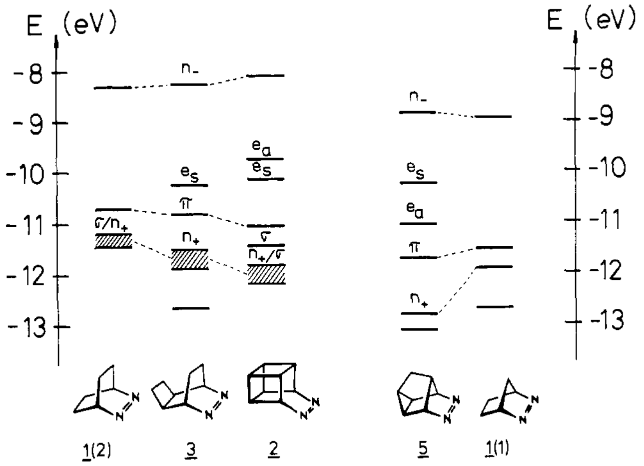


Figure 6. Correlation of the highest occupied MO's for **1**(1), **1**(2), **2, 3,** and **5**.

π(NN) deserves comment. It appears as though semiempirical SCF-MO methods often produce unstable σ orbitals when π orbitals are present in the molecule.[31] The location of the high-lying a″ MO may be ascribed to this effect.

The identification of n_+ with the peak at 11.7 or with the one at 12.7 eV remains. The latter choice would imply that the n_-/n_+ splitting is ca. 1 eV greater in **3** than in **2** and that n_+ is stabilized by 1.4 eV as compared to **1**(2). Neither our calculations nor the stabilizing influence of cyclopropane on n_+ ($\leq$0.9 eV, see below) are supportive. Therefore we conclude that it is quite likely that the n_+ lone pair contributes to the band observed at 11.7 eV. A summary of the MO distribution for **1**(2), **2**, and **3** is given in Figure 6.

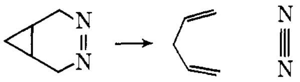
Assignment of the Diazadeltacyclene PE Spectrum

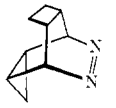
The first band is again assigned to the removal of an electron from the antisymmetric combination of lone pair orbitals n_-. Unfortunately the PES of deltacyclene **10** has not been reported, and therefore, the empirical correlation employed to assist with the assignment of the π band in diazabasketene cannot be applied directly to **5**. However, the π IP (8.9 eV) for tricyclo[3.2.1.0^{2,4}]oct-6-ene[29] (**9**) can be used to estimate an expectation value for the corresponding IP of **10**. Table III lists nitrogen extrusion rates for the isoelectronic azoalkanes **4** and **5**, respectively, and indicates the drastic change as a function of ancilliary bridge size and dihedral angle (θ, **16**). An experimental correlation[11] between θ and the π(NN) IP implies that the latter should increase by at least 0.2 eV upon passage from **4** to **5**. CNDO[25] optimization of θ for the latter leads to values of 123 and 97°, respectively. A stabilization of 0.36 eV for the π(NN) orbital in **4** (−10.55 eV) relative to **5** (−10.19 eV) is predicted.

Thus if the effect of reducing θ by adding a -CH$_2$- link is to diminish the cyclopropyl interaction by about 0.4 eV, then the π IP of **9** suggests that the π IP of **10** should be at about 9.3 eV. This in turn suggests, by the empirical correlation mentioned above, that the π band of diazadeltacyclene (**5**) should lie in the region 10.9 to 11.9 eV, with a preference for the upper part of the range since **5** is a quite rigid molecule. Accordingly we assign the fourth band (11.73 eV) in the PE spectrum to the π orbital of **5**.

As in the case of diazabasketene, we have carried out several MO calculations for diazadeltacyclene. We assumed C_{2v} symmetry for the former. This means that the n_+, π, and n_- orbitals transform according to the a_1, b_1, and b_2 irreducible representations, respectively. The highest possible symmetry of **5** is C_s and, therefore, the MO's are classified as a′ (n_+ and π) or a″ (n_-). Our calculations[25] (cf. Table II) yield, in order of increasing binding energy, the following MO configuration: a″, a′, a′, a″, a″, a′, plus inner orbitals (the latter two orbitals are interchanged by one set of CNDO parameters). The first MO is easily recognized as the n_- lone pair orbital. The second MO and to a lesser extent the third MO of a′ symmetry involve π bonding between the nitrogen atoms as well as possessing large contributions from the two equivalent carbon atoms of the three-membered ring. The mixing is strong but we can identify the highest a′ level as the π(NN) MO and the more stabilized one as the e_s orbital of the cyclopropane degenerate pair.[33] The fourth a″ MO has very little electron density on nitrogen and resembles the cyclopropane e_a orbital. The fifth energy level is easily recognized as the n_+ lone pair orbital. Thus the MO calculations favor the second band as the π IP whereas the empirical correlations discussed above favor the fourth band. To resolve this situation it is necessary to consider the MO calculations in greater detail.

Table III. Relative First-Order Rates for the Extrusion of Nitrogen (−3.5 °C)[a]

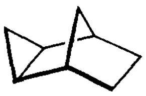


Compd	Solvent	$10^4 \times k_1$, s^{-1}
4[b]	CDCl$_3$	1
17 (n = 1)[c]	Pyridine/CuCl	2.2
16 (n = 3)[d]	CDCl$_3$	0.9
(n = 2)[d]	CDCl$_3$	2.5×10^{-3}
(n = 1),[d] **5**	CDCl$_3$	4.3×10^{-11}
17 (n = 2)[c, e]	Gas phase	1.2×10^{-12}
	Gas phase[e]	1.6×10^{-14}
19[f]	Hexachloro-butadiene	(>155 °C dec)

[a] Gas phase measurements extrapolated to −3.5 °C; cf. ref 22a and 43 for control experiments comparing solution and gas phase azo decomposition. [b] E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Am. Chem. Soc.*, 91, 3382 (1969), and ref 43. [c] Reference 22a. [d] Reference 43. [e] Reference 38. [f] B. M. Trost and R. M. Cory, *J. Am. Chem. Soc.*, 93, 5573 (1971).

Our calculations suggest, according to Koopmans' theorem, that the first IP of cyclopropane is greater than the IP for the removal of a π(NN) electron from **1**(1) (11.0 and 10.9 eV, respectively) contrary to the observed values of 11.0[34] and 11.5[10] eV, respectively. Consequently if diazadeltacyclene is described in terms of the interactions between localized orbitals of cyclopropane and **1**(1), then the result of mixing the π(a′) orbital of **1**(1) and the e_s orbital (also of a′ symmetry in **5**) would be to destabilize the π orbital and to stabilize the e_s orbital. This is precisely what happens in the three MO calculations we have performed.

The origin of the inverted, predicted order of the e_s and π(NN) orbitals can be understood by considering experimental IP's and comparing them with the results of model calculations. Alkyl substitution of cyclopropane lowers the IP's of both e_s and e_a.[29] For example, the values for the saturated tricycle **13** are found at 9.4 and 10.0 eV, respectively. The cyclopropane unit found in deltacyclane (**14**) should experience similar IP adjustment. For **14** we calculate that the e MO values fall at 9.7 and 10.0 eV in accord with expectation.



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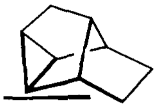

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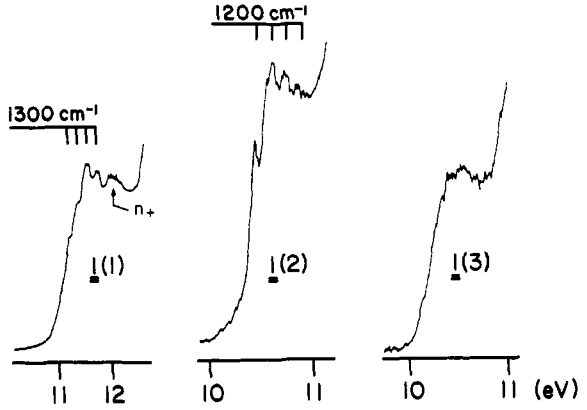


Figure 7. Second band of photoelectron spectrum of **1**(*n*), *n* = 1, 2, 3.

The corresponding levels in diazadeltacyclene (**5**) will be characterized by higher calculated IP's (10.7 and 11.1 eV, cf. Table II) in part as a consequence of the inductive effect of the $-N{=}N-$ bridge. Unfortunately the ionization potential for the latter appears to be less satisfactorily reproduced by the CNDO/INDO schemes utilized in the present work. For example, as mentioned above, the π(NN) IP of **1**(1) is overestimated by 0.6 eV. Other bicyclo [2.2.1] cases (e.g. **19**) are similarly valued upward (e.g., **5**, +1.6 eV; **19**, +1.2 eV) leading to the result that π(NN) in **2** is most likely pulled artificially below e_s. It appears, therefore, that while the relative values of hydrocarbon and hydrocarbon-fragment IP's may be qualitatively reproduced by semiempirical schemes,[23a,31b,35] the introduction of strongly electronegative atoms can, in certain cases, lead to completely misleading predictions.

In view of this analysis we conclude that the MO calculations incorrectly place the π orbital above the e_s orbital and that the first five bands of the PE spectrum of diazadeltacyclene are assigned as follows: 8.83 (n_-), 10.25 ($\sigma(e_s)$), 11.06 ($\sigma(e_a)$), 11.73 (π), and 12.8 (n_+). Schweig, Trost, and coworkers[11] have recently arrived at the same conclusion. It is interesting to note that this is very similar to our assignment for diazabasketene in that two σ bands are observed between the n_- and π bands (cf. Figure 6).

Further Remarks on the Assignment of the PE Spectra of **1**(*n*)

The position and shape of the first band of the PE spectra of **1**(*n*) (see Figure 1 of ref 10) are quite characteristic for the ionization of a lone pair orbital, namely the antisymmetric combination n_-. We have previously assigned[10] the second band of these spectra as arising from the ionization of the π(NN) orbital. The above discussion for **2**, **3**, and **5** shows that high-lying σ-type orbitals may have a lower IP than the π(NN) orbital. The following question thus arises: can such a situation also occur for **1**(*n*)? The second band of the PE spectra of both **1**(1) and **1**(2) exhibits fine structure (1300 and 1200 cm^{-1}, respectively, assigned to $\nu_{N=N}$[10]) as shown in Figure 7 and there is little reason to doubt the assignment of this band to the ionization of a π orbital even though the MO calculations for **1**(2) do not reproduce this ordering (cf. Table II).[49] The symmetry imposed for the MO calculations for **1**(2) was C_{2v}. Molecular models show however that **1**(2) is a somewhat flexible molecule. In the C_{2v} form both carbon bridges involve four eclipsed hydrogens. Such a structure probably stabilizes the π level by permitting a more effective mixing of the carbon framework orbitals in a bonding way, as shown by population analysis of the calculations for **1**(1) and **1**(2). Rotation around the C-C bridges (**15**) removes the destabilizing interactions between the hydrogen atoms. In turn this leads to a loss of the favorable overlap between the C_{2p} orbital contributions with a consequent increase in the energy of the π orbital.

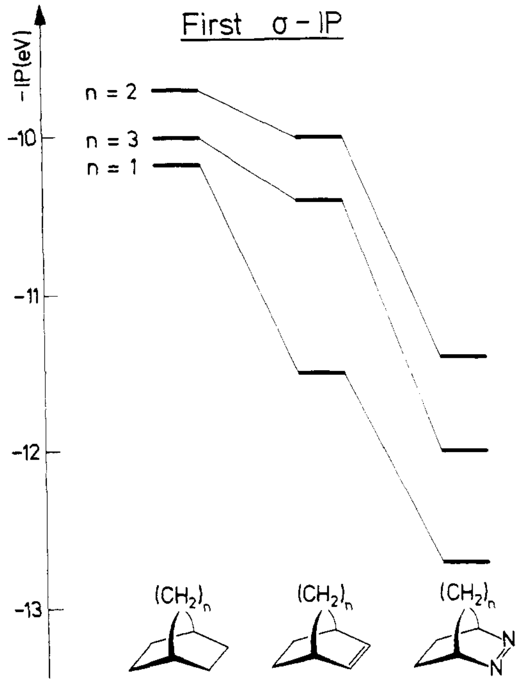
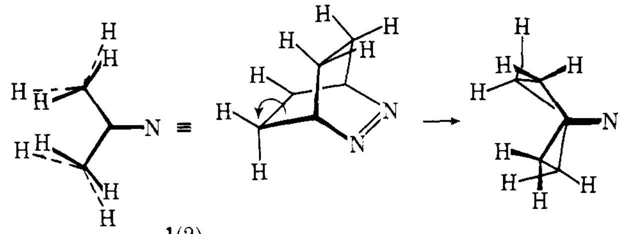


Figure 8. Correlation of the first σ IP of bicyclo[2.2.*n*]alkane, bicyclo-[2.2.*n*]alk-2-ene, and **1**(*n*) for *n* = 1, 2, 3.



1(2)

15

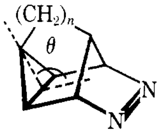
In the solid state **1**(2) does not in fact possess C_{2v} symmetry.[36] The C-C dihedral angles are small (5.3 ± 0.2 °C) but nonetheless real. Vapor of **1**(2) analyzed in the PES experiment may well consist largely of unsymmetrical conformers **15** rapidly interconverting over a shallow energy barrier.[37] In accord with this analysis the rigidified [2.2.2] framework of **3** yields a π level stabilization of 0.17 eV (cf. **1**(2) and **3** in Table I and Figure 6).

The second band of the PE spectrum of **1**(3) also appears to possess fine structure although a definitive conclusion cannot be drawn due to a poorer signal-to-noise ratio (see Figure 7); no such structure is evident for **1**(4). In the absence of other experimental evidence it is difficult to assign with certitude this second band. We believe however that our original assignment is correct and we can substantiate it, at least for **1**(3), by pointing out that the variation of the first σ IP in the series going from the bicyclo[2.2.*n*]alkane to the bicyclo[2.2.*n*]alk-2-ene (**6**(n)) and to **1**(*n*) is quite similar for *n* = 1, 2, and 3, provided the first σ IP of **1**(3) is assigned to the shoulder at 12.0 eV (see Figure 8).

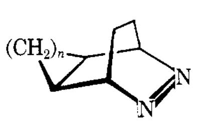
As will be discussed in the last section of this paper, there is strong mixing of the MO's, especially for molecules of low symmetry. Hence we conclude that labels such as σ and π are somewhat arbitrary and that it is not contradictory to have a n_-, π, n_+, σ, . . . ordering for **1**(*n*) and an n_-, σ, σ, π, . . . one for **2** and **5**.

Homoconjugation and Reactivity in Polycyclic Azoalkanes

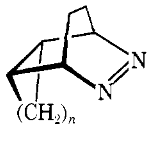
The relative rates of nitrogen extrusion from polycyclic azoalkanes have been investigated for systems represented



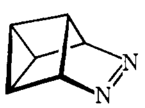
16, n = 1-3



17, n = 1,2



18, n = 1,2



19

by structures **16–19** (cf. Table III).

The essential findings are that the first-order rates are significantly enhanced for anti vs. syn ring fusion (**17** $\gg$ **18**),[22a,38,39] for cyclopropyl relative to cyclobutyl substitution (n = 1 $\gg$ n = 2),[40–42] and for an increased dihedral angle, θ.[43] The anti-cyclopropanated azo derivatives thus meet the criteria[42] for synchronous three-ring opening and nitrogen departure and underline the dominance of electronic effects in the transition state.[41,42] Specifically it appears that the geometric disposition of orbital components for a small ring which provides for maximum overlap with the incipient C–N bond leads to the greatest rate increases. Recently the rate variation was rationalized[11] as a function of θ by evaluating the PE spectra of compounds **1**(1), **5**, and **19**. The authors concluded that increased values of θ lead to increased homoconjugation between the -N=N- bridge and the *anti*-cyclopropyl ring in the ground state. The homoconjugative interaction was assumed to be reflected in the corresponding transition states for nitrogen expulsion.

For unsaturated polycyclic hydrocarbons containing three- and four-membered rings (e.g., **8** and **9**) three criteria have evolved as a measure of homoconjugation: ΔE(e$_s$–π),[23c,29] ΔE(e$_s$–e$_a$),[30] and E_π.[30] The first and second quantities require the PE spectra of model compounds similar in skeletal structure but lacking the C=C double bond. The third criterion calls for a model π system unsubstituted by small rings. Homoconjugation in diazadeltacyclene (**5**) can be inferred from the latter by reference to Figure 6. Both π(NN) and n$_+$ are stabilized relative to **1**(1).

The criteria involving e$_s$ are more difficult to apply since the PE spectrum of deltacyclane (**14**) has not been recorded. Furthermore corrections for the inductive effect of the N=N bridge are not yet available. Cyclopropane ionization potentials are unsuitable since fusion of the three-carbon ring onto a bicycle raises the MO energies of e$_s$ and e$_a$ by ca. 1.5 and 0.9 eV, respectively.[29,44] Nonetheless measurements[11] comparing **5** and **19** assure that the e$_s$ criteria are operational in the cyclopropyl azo series as well.

Fusion of a cyclobutane ring onto **1**(2) leads to a stabilization of π(NN) ($\Delta\pi$ = −0.17 eV) and n$_+$. (Δn$_+$ = −0.5 eV) somewhat less than for the corresponding levels of diazaquadricyclene (**5**) relative to **1**(1) ($\Delta\pi$ = −0.20 eV, Δn$_+$ = −0.9 eV) (cf. Figure 6). The reduced influence of cyclobutane vs. cyclopropane on molecular ionization potentials is also evident in all-carbon polycycles.[23c,30] However, as pointed out with reference to structure **15**, the source of the stabilization for the three- and the four-membered compounds may be different. Attachment of a cyclopropane to the rigid [2.2.1] framework leads to a purely homoconjugative stabilization of π(NN) and n$_+$. Similar fusion of a cyclobutane onto the more flexible [2.2.2] skeleton rigidifies the system and possibly allows for a more favorable mixing of -N=N- orbitals with the entire carbon framework. Thus the observation of a weak π(NN)/n$_+$ stabilization may, in fact, imply an even smaller through-space interaction of the azo unit and the four-membered ring. If the correlation between ground-state homoconjugation and relative nitrogen extrusion rates is valid, this interpretation is consistent with the conclusion that azo **3** thermolyzes slowly by a diradical pathway.[40] It should be noted, however, that the π(NN)/n$_+$ level stabilization in **3** is small even when taken as a whole and could well lie below the limit necessary for translation into an influential transition state interaction.

In the above discussion two empirical correlations have been mentioned: (1) between the dihedral angle (θ, **16**) of ground-state cyclopropanated azo compounds and thermal decomposition rates (Table III), and (2) between θ and the ionization potentials (e$_s$, π(NN), and n$_+$) for **1**(1), **5**, and **19**.[11] A question of some importance is the validity of the corollary relationship between high-lying MO energies and reaction rates; namely is the interdependence fundamental or fortuitous? It has been argued that cyclopropane bond breaking and -N=N- bond making in the transition state are in qualitative accord with e$_s$ destabilization and π(NN)/n$_+$ stabilization in the ground state as θ increases.[11] An implicit assumption in this view is that the high-lying π(NN) (IP = ca. 11.5 eV) and n$_+$ (IP = 12-13 eV) molecular orbitals in fact correlate with the low-lying bonding MO's of molecular nitrogen (IP$_1$ = 15.6 eV, IP$_2$ = 16.7 eV).[45] In the absence of the necessary MO transformations, a minimum alternative requirement within the framework of an MO description is that the energetic behavior of the azoalkane MO's in question parallel the relative ground-state MO energies *at least up to* the transition state.

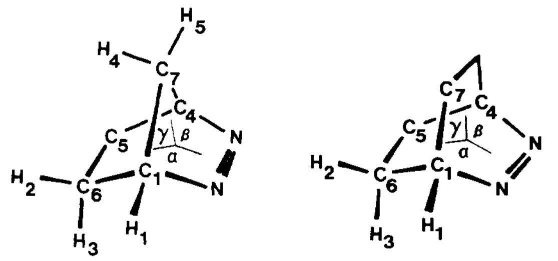
Preliminary potential surface calculations for pericyclic azoalkane decomposition[32] lead to the result that n$_-$, π(NN), and n$_+$ do not correlate with N$_2$ MO's, but are gradually permuted instead into hydrocarbon orbitals. Lower lying azo energy levels with large nitrogen contributions (cf. interpretation section below) correlate with high-lying N$_2$ levels. The implication is that while the distribution of outer azo orbitals reflects the kinetic sequence, the favorable relationship may be coincidental. This point is under scrutiny.

Molecular Geometries

In our previous discussion[10] of the PES of *cis*-azoalkanes we mentioned several CNDO calculations for molecules whose structural parameters were unknown. The calculations were based on assumed geometries. This procedure is subject to the risk, in addition to the limitations[46] associated with Koopmans' theorem, that the ordering of the MO's may be sensitive to changes in the molecular geometry. In order to assess the accuracy of the assumed geometries and to investigate the effect of geometry on the MO's, additional CNDO calculations were made using a parameterization[25] which was specifically developed to yield molecular potential surfaces which agree relatively well with experimental results at the minimum, that is, the equilibrium geometry.

The calculated equilibrium geometries for the two bicyclic molecules **1**(1) and **1**(2) are shown in Table IV and compared with x-ray[36] and preliminary microwave[47] structures determined after completion of our work. The calculated N=N and N—C bonds are shorter than the experimental values by 0.03-0.05 and 0.08-0.1 Å, respectively. The same discrepancy obtains by comparison with a series of *trans*-alkyl derivatives (r(N=N) = 1.217-1.253 Å;

Table IV. CNDO[25] Optimized Geometries and Experimental Structures for **1**(1) and **1**(2) (r(AB), Å; ∠ABC, deg)



	1(1)		**1**(2)	
	CNDO optimized	Micro-wave[47]	CNDO optimized	X ray[36]
r(NN)	1.21	1.246	1.21	1.260
r(CN)	1.41	1.506	1.40	1.487
$r(C_1C_6)$	1.59	1.538	1.58	1.542
$r(C_1C_7)$	1.59	1.534	1.58	1.542
$r(C_5C_6)$	1.58	1.552	1.57	1.533
r(CH)	1.10	1.10	1.10	
$r(C_1-C_4)$	2.22	2.192	2.56	2.503
∠CNN	110.9	108.3	118.9	114.7
$\angle C_1C_6C_5$	101.7	102.1	108.1	108.5
$\angle C_6C_1N$	102.4		104.2	108.5
$\angle C_6C_1C_7$	105.1	103.1	113.4	109.9
$\angle C_7C_1N$	98.5	100.4	104.2	106.8
$\angle C_1C_7C_4$	88.7	91.3		
$\angle H_1C_1N$	110.1	110.7	103.9	107.3
$\angle H_1C_1C_6$	117.4	117.1	114.7	112.2
$\angle H_1C_1C_7$	120.2	119.6	114.7	111.8
$\angle H_2C_6C_1$	111.0	110.9	109.8	109.6
$\angle H_2C_6C_5$	112.5		111.0	112.7
$\angle H_3C_6C_1$	111.0	110.6	109.8	107.0/107.9
$\angle H_4C_7C_1$	114.3	112.4		
$\angle H_2C_6H_3$	108.1	108.2	107.1	107.5/110.7
$\angle H_4C_7H_5$	109.8	111.4		
α	108.4	109.0	120.4	122.5
β	126.5	127.7	119.3	122.5
γ	88.7	91.3	121.8	120.3

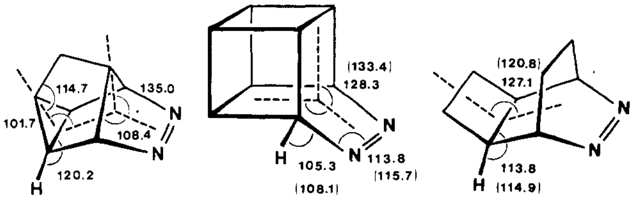


Figure 9. Partially optimized geometries for diazadeltacyclene (**5**) (C_s), diazabaskentene (**2**) (C_{2v}) and cyclobutane (**3**) (C_s). Parenthetical values have been experimentally determined.[36]

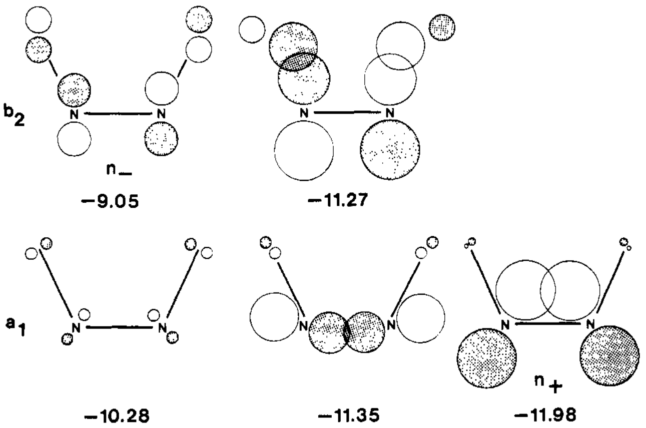


Figure 10. Partial CNDO[25] eigenfunctions for the high-lying b_2 and a_1 MO's of diazabasketene (**2**) as a function of energy. Only the nitrogen bridge and bridgehead carbon contributions are shown. Circle radii represent the squares of the relative atomic orbital components among the five MO's pictured.

r(C–N) = 1.474–1.501 Å).[48] By contrast C–C bond lengths are predicted to be too long by 0.02–0.06 Å.

In spite of the fair to moderate agreement obtained for bond distances, bond angles are very accurately reproduced. The average deviations for **1**(1) and **1**(2) are only 1.2 and 2.7°, respectively. The lower accuracy for **1**(2) is undoubtedly a result of the C_{2v} symmetry assumed in the calculation.

For compounds **2**, **3**, and **5** the energy was minimized with respect to only a few structural parameters. These are indicated in Figure 9. The remainder are based on the calculated equilibrium geometries or assigned "standard" values. Although no experimental data are available for diazadeltacyclene, the experimental angles are adequately reproduced for substances **2** and **3**.

Comparison of CNDO calculations for **1**(1) with the two different parameterizations[24,25] used in this work indicates that essentially the same MO scheme is obtained with the calculated equilibrium or the experimental geometries as was obtained previously by use of assumed geometries. Likewise diazadeltacyclene "standard" and minimized structures yield the same relative set of energy levels. However, some changes are observed for **1**(2). With the assumed geometry CNDO/2[24] yields −11.10 (b_2), −13.94 (a_2), −14.04 (a_1), and −14.06 (b_1) for the four highest occupied MO's, but with the optimized geometry shown in Table IV the orbital energies become −11.21 (b_2), −13.55 (a_1), −14.13 (b_1), and −14.35 (a_2) (cf. column 2 of Table II where the a_2 remains above the b_1 MO). For the reasons we have already discussed, the second band of the PE spectrum of **1**(2) is assigned to the ionization of the π(NN) orbital, that is the highest b_1 MO, and not to a high-lying σ orbital, such as the highest occupied a_2 and a_1 MO's listed above.

Interpretation of PE Spectra by MO Calculations

To conclude our discussion we would like to comment on a problem associated with the interpretation of the PE spectra of relatively complex molecules by MO calculations. For simplicity we consider *cis*-azo molecules with C_{2v} symmetry.

In a simple molecule, such as diazirine, there are very few MO's of each symmetry type (irreducible representations) and it is a relatively simple problem to classify the MO's. Thus from the eigenvectors for an all-valence-electron calculation on diazirine it is easy to decide which of the two b_2 MO's is the n_- lone pair orbital, which of the two b_1 MO's is the π orbital, and which of the four a_1 MO's is the n_+ lone pair orbital.

As the molecular size increases the number of MO's and the degree of delocalization tend to increase and it becomes more difficult to separate the lone pair orbitals from the MO's which constitute the σ framework. This is illustrated by the molecules studied in this paper. For example, the highest occupied b_2 MO in diazabasketene is less localized on the nitrogen atoms than the next highest b_2 MO which lies several eV below (cf. Figure 10). If the n_- lone pair were taken to be the b_2 MO most highly localized on the nitrogen atoms then the first band in the PE spectrum of diazabasketene would be assigned to a σ MO and one of the inner IP's, perhaps the sixth, would be assigned to the n_- lone pair. However, this would imply that the n_- lone pair which gives rise to the first band in the PE spectra of simple *cis*-azo molecules would be abruptly stabilized by several electron volts as the molecular size increases. Thus a correlation diagram for the n_- lone pair in *cis*-azo molecules would display what we might refer to as a "discontinuity" as a function of the size and complexity of the molecule.

A similar but reversed situation arises for the a_1 MO's in diazabasketene. The degree of localization on the nitrogen atoms increases as the binding energy increases for the first three a_1 MO's. As outlined earlier, we assign the first and the second to high-lying σ orbitals and the third to the n_+ lone pair. In this case the lone pair has been assigned to the MO with the appropriate symmetry and most highly localized on the nitrogen atoms. To have chosen either of the upper a_1 levels would have implied a sudden destabilization of the lone pair as the molecular size increases.

This situation, which has not been discussed elsewhere as far as we are aware, is not peculiar to *cis*-azo molecules but will arise for all types of molecules which have lone pair orbitals. Nor is it unique to the C_{2v} point group. In general we suggest that the lone pairs of relatively large molecules not be assigned solely on the basis of maximum localization, but rather it is also important to relate the lone pair orbitals to simpler but closely related molecules so that "discontinuities" of the kind we have discussed are avoided.

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References and Notes

(1) The IUPAC nomenclature is 7,8-diazapentacyclo$[4.2.2.0^{2,5}.0^{3,9}.0^{4,10}]$dec-7-ene for diazabasketene and 6,7-diazatetracyclo$[3.2.1.1^{3,8}.0^{2,4}]$non-6-ene for diazadeltacyclene.
(2) (a) University of British Columbia; (b) H. C. Orsted Institute.
(3) (a) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971); (b) R. Hoffmann, *ibid.*, **4**, 1 (1971); (c) R. G. Pearson, *ibid.*, **4**, 152 (1971); *J. Am. Chem. Soc.*, **94**, 8287 (1972).
(4) H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); **5**, 393 (1972); M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971); W. A. Goddard, *J. Am. Chem. Soc.*, **94**, 793 (1972); C. Trindle, *ibid.*, **92**, 3251, 3255 (1970).
(5) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(6) D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys. Lett.*, **30**, 26 (1975).
(7) E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, **81**, 897 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 878 (1969); E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970).
(8) M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *J. Chem. Phys.*, **51**, 45 (1969).
(9) (a) F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung, and D. M. Lemal, *Helv. Chim. Acta*, **56**, 1933 (1973); (b) K. N. Houk, Y. M. Chang, and P. S. Engel, *J. Am. Chem. Soc.*, **97**, 1824 (1975).
(10) R. J. Boyd, J. C. Bünzli, J. P. Snyder, and M. L. Heyman, *J. Am. Chem. Soc.*, **95**, 6478 (1973).
(11) H. Schmidt, A. Schweig, B. M. Trost, H. B. Neubold, and P. H. Scudder, *J. Am. Chem. Soc.*, **96**, 622 (1974).
(12) S. F. Nelsen and J. M. Bushek, *J. Am. Chem. Soc.*, **96**, 6987 (1974).
(13) P. Rademacher, *Tetrahedron Lett.*, 83 (1974); *Angew. Chem.*, **85**, 410 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 408 (1973).
(14) J. C. Bünzli, D. C. Frost, and C. A. McDowell, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 481 (1972).
(15) D. R. Lloyd, *J. Phys. E*, **3**, 629 (1970).
(16) J. P. Snyder, V. T. Bandurco, F. Darack, and H. Olsen, *J. Am. Chem. Soc.*, **96**, 5158 (1974).
(17) Cf. J. P. Snyder, L. Lee, and D. G. Farnum, *J. Am. Chem. Soc.*, **93**, 3816 (1971).
(18) M. Heyman, V. T. Bandurco, and J. P. Snyder, *Chem. Commun.*, 297 (1971).
(19) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).
(20) J. P. Snyder, L. Lee, V. T. Bandurco, C. Y. Yu, and R. J. Boyd, *J. Am. Chem. Soc.*, **94**, 3260 (1972).
(21) J. P. Snyder, M. L. Heyman, and E. N. Suciu, *J. Org. Chem.*, **40**, 1395 (1975).
(22) (a) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969); (b) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341 (1969); R. Askani, *Chem. Ber.*, **102**, 3304 (1969).
(23) (a) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, **92**, 19 (1970); (b) P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969); (c) P. Bruckman and M. Klessinger, *Angew. Chem.*, **84**, 543 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 524 (1972).
(24) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
(25) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73 (1972).
(26) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(27) R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971).
(28) W. Schmidt and B. T. Wilkins, *Tetrahedron*, **28**, 5649 (1972).
(29) P. Bischof, E. Heilbronner, H. Prinzbach, and H. D. Martin, *Helv. Chim. Acta*, **54**, 1072 (1971).
(30) H. D. Martin, S. Kagabu, and R. Schwesinger, *Chem. Ber.*, **107**, 3130 (1974).
(31) E.g. (a) M. J. S. Dewar, E. Haselbach, and S. D. Worley, *Proc. R. Soc. London, Ser. A*, **315**, 431 (1970); M. Beez, G. Bieri, H. Bock and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973); C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 333 (1972/73); N. Bodor, B. H. Chen, and S. D. Worley, *ibid.*, **4**, 65 (1974); (b) R. C. Bingham, M. J. S. Dewar, and D. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975).
(32) J. P. Snyder, to be published.
(33) A. D. Walsh, *Nature* (*London*), **159**, 167, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949); cf. ref 34.
(34) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).
(35) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970); L. Åsbrink, C. Fridh, and E. Lindholm, *ibid.*, **94**, 5501 (1972); it should be noted that while MINDO-3 first IP's for hydrocarbons are within 0.65 eV of experiment,[31b] the corresponding values for oxygen and nitrogen containing compounds have not been reported: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *ibid.*, **97**, 1302 (1975).
(36) X-ray analysis: T. Ottersen, C. Romming, and J. P. Snyder, *Acta Chem. Scand.*, in press.
(37) Y. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 2017 (1970).
(38) E. L. Allred and K. J. Voorhees, *J. Am. Chem. Soc.*, **95**, 620 (1973).
(39) L. A. Paquette and L. M. Leichter, *J. Am. Chem. Soc.*, **92**, 1765 (1970); **93**, 4922, 5128 (1971).
(40) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972).
(41) L. A. Paquette and M. J. Epstein, *J. Am. Chem. Soc.*, **95**, 6717 (1973).
(42) J. A. Berson, S. S. Olin, E. W. Petrillo, and P. Bickart, *Tetrahedron*, **30**, 1639 (1974).
(43) E. L. Allred and A. L. Johnson, *J. Am. Chem. Soc.*, **93**, 1300 (1971).
(44) The apparent correlation[11] of cyclopropane e_s and e_a MO's with the corresponding levels of **5** and **19** arises from a fortuitous cancellation of cyclopropane substitution effects[29] and the nitrogen inductive effect.
(45) D. W. Turner and D. P. May, *J. Chem. Phys.*, **45**, 471 (1966).
(46) W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).
(47) R. Suenram (Harvard University), submitted for publication.
(48) A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 1230 (1970); C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 5313 (1970); G. Argay and K. Sasvari, *Acta Crystallogr.*, **27**, 1851 (1971); A. B. Jaffe, D. S. Malament, E. P. Slisz, and J. M. McBride, *J. Am. Chem. Soc.*, **94**, 8515 (1972), and references therein.
(49) PRDDO calculations[50] are supportive; the calculated MO energies (eV) and the assignment obtained by using experimental geometries are: -9.14 (n_-), -11.38 (π), and -12.31 (n_+) for **1**(1); and -8.36 (n_-), -11.22 (π), and -11.53 ($n_+ + \sigma$) for **1**(2).
(50) T. A. Halgren and W. M. Lipscomb, *J. Chem. Phys.*, **58**, 2569 (1973).