Dioxetenes and Diazetines: Nonaromatic 6π-Systems in Four-Membered Rings

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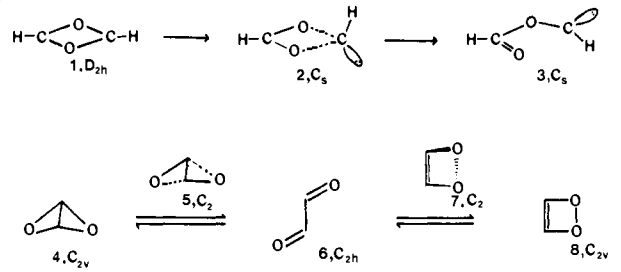
Abstract: The potentially 6π-aromatic dioxetenes and diazetines were studied by ab initio MO methods. The electron density distributions in these molecules were analyzed to obtain insight into the details of the bonding. None of the species shows any evidence for a stabilizing 6π-delocalization. The 1,2-dioxetenes and 1,2-diazetines have completely localized C=C double bonds and normal C—X and X—X single bonds (X = O, NH). The conrotatory ring-opening reactions of these molecules to glyoxal or to α-diimine are highly exothermic and have lower activation energies than the similar conversion of cyclobutene to butadiene. In principle, two electronic configurations are possible for the 1,3-dioxetenes and 1,3-diazetines, differing in the occupation numbers of the π-orbitals π_1–π_4. The "aromatic" occupation $\pi_1^2\pi_2^2\pi_3^2$ produces nearly square structures but these show no evidence of strong C—X π-bonding. Furthermore, they are unstable with respect to symmetry lowering: optimization in C_s symmetry results in $HCX_2^-\cdots CH^+$ complexes. For X = O, the complex opens without activation energy to (formyloxy)methylene. For X = NH, the ring opening has a considerable activation energy. Hence, 1,3-diazetines, though highly reactive and not aromatic, might be experimentally accessible. The alternative $\pi_1^2\pi_2^2\pi_4^2$ configuration produces highly strained dioxa- and diazabicyclobutanes with unusually short C—C bonds; they have appreciable π-complex character. The oxygen compound ("acetylene diepoxide") is predicted to collapse to glyoxal without an activation barrier, but the nitrogen analogue should be more stable.

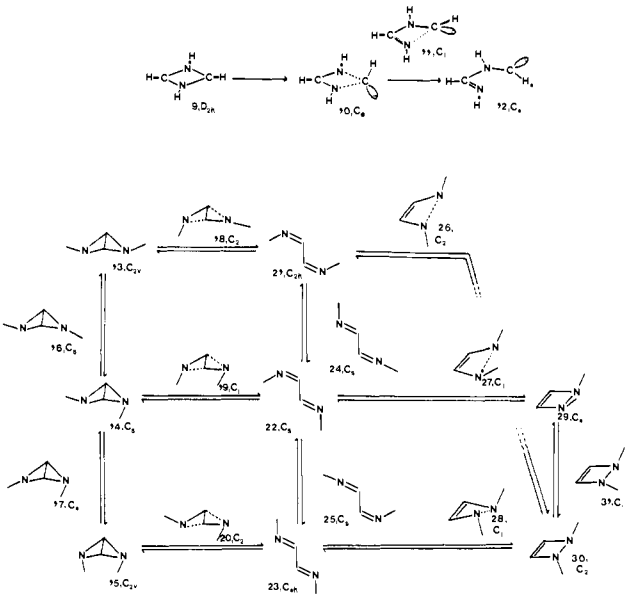
According to the Hückel $(4n + 2)/4n$ rule, four-membered-ring compounds should be aromatic with 2 or 6 π-electrons and antiaromatic with 4 π-electrons.[2] Despite these predictions, few four-membered-ring 6π-systems are known. The instability of the 6π cyclobutadiene dianion has been attributed to the large negative charge per carbon atom[3] and more recently also to the strong 1,3-repulsive interactions in the π-system.[4,5] The isoelectronic neutral dioxetenes $(CHO)_2$ and diazetines $(CHNH)_2$ suffer less from electrostatic repulsions and might be expected to be more favorable. The repulsive interactions in the π-system remain, however, and we explore their consequences in this paper. The structures of 1,3-diazetine, 1,2-diazetine, and diazabicyclobutane have already been studied at the MINDO/3 level by Minyaev and Minkin.[6]

It is instructive to inspect the π-orbitals of these heterocycles (Figure 1) in some detail. The lowest π-orbital, π_1, is overall bonding. The next two orbitals, π_2 and π_3, are 1,2-nonbonding and 1,3-antibonding. The remaining π-orbital, π_4, is 1,2-antibonding and 1,3-bonding. Carbocycles that have only π_1 occupied are aromatic ($C_4H_4^{2+}$,[7] $C_2B_2H_4$[8]). Adding more π-electrons does *not* increase the peripheral bond strengths, since π_2 and π_3 are 1,2-nonbonding. Rather, the 1,3-antibonding nature of these orbitals results in a *decrease of π-bonding*.

Scheme I



Scheme II



In $C_4H_4^{2-}$, π_2 and π_3 are degenerate. The introduction of the more electronegative NH or O groups in the 1,3-positions lifts this degeneracy by lowering the energy of π_1, π_2, and π_4 (Figure

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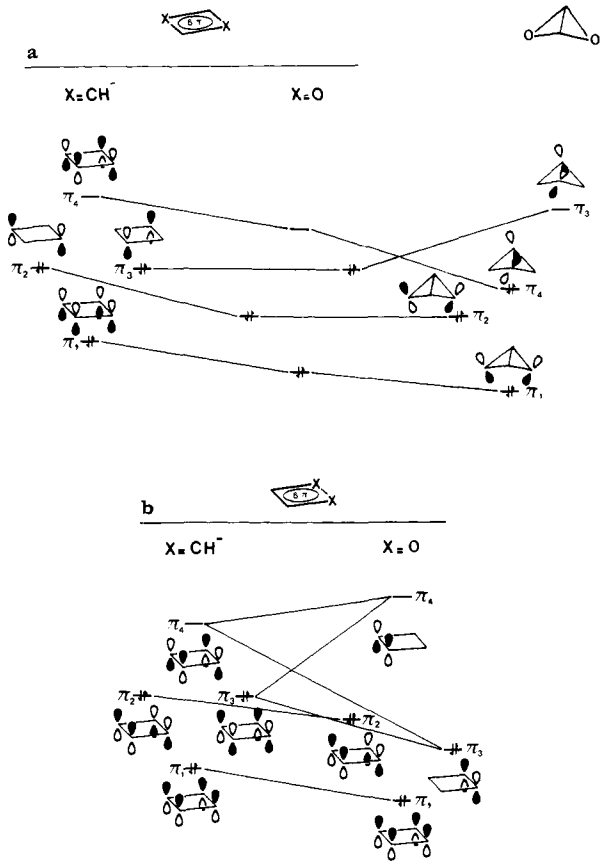
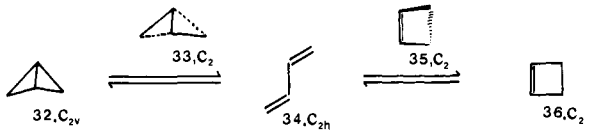


Figure 1. Schematic representations of the four π-orbitals of 1,3-$(CHX)_2$ (a) and 1,2-$(CHX)_2$ (b) species.

Scheme III



1a); π_3 is hardly affected since it has a node at the X atoms. Since π_4 is 1,3-bonding, it will be lowered even more by puckering and might end up below π_3. Populating π_4 instead of π_3 will result in a puckered bicyclobutane-like structure. Thus, the "aromatic destabilization" can be partly avoided at the expense of increased ring strain. Introducing the heteroatoms in the 1,2-positions not only removes the degeneracy of π_2 and π_3 but also enables mixing of π_3 with π_4 (Figure 1b). If the X atoms are fairly electronegative, this mixing can result in a localized structure having a C=C double bond and an X—X single bond.

A few 1,2-diazetines have been reported;[9,10] they are rather unstable and are apparently not aromatic. 1,2-Dioxetenes have been proposed as unstable intermediates in the oxidation of highly reactive acetylenes with singlet oxygen.[11]

This paper focuses on the stabilities of the 6π-heterocycles dioxetene and diazetine and of their open-chain isomers glyoxal and α-diimine, and considers the possible reaction pathways connecting these isomers. The most important reactions, sketched in Scheme I for dioxetene and in Scheme II for diazetine, are ring-opening reactions that have their counterparts in the chemistry of the carbocyclic $(CHCH_2)_2$ systems cyclobutene and bicyclobutane (Scheme III). Therefore, we have also included the carbon compounds for comparison. The conrotatory opening of cyclobutene has been studied in detail by Schaefer.[12] The ring opening of bicyclobutane[13,14] probably proceeds by an asymmetric, two-step biradical pathway.[15] For comparison with the oxygen and nitrogen compounds, however, we have calculated the "transition state" corresponding to concerted opening in C_2 symmetry.[16]

In the first part of the paper, we use calculated energies and geometries to discern some trends in the stabilities of the various species. In the second part, we interpret these trends using a detailed picture of the molecular structure, obtained from analyses of the electron density distributions. Finally, the relevance of our theoretical results to the stability of 6π-systems will be discussed.

Methods

The geometries of **1–36** were optimized completely,[17] subject only to overall molecular symmetry constraints, at the closed-shell restricted Hartree–Fock[18] (RHF) level using the small split-valence 3-21G basis set.[19] Where doubt existed, stationary points were characterized as local minima, transition states, or higher order saddle points by the number of negative eigenvalues of the Hessian matrix (zero, one, or more than one, respectively).[20] The numbers of negative eigenvalues (at the 3-21G level) are given in Table II. The geometries of the oxygen compounds **1–8** were reoptimized by using the larger split-valence + polarization 6-31G* basis set.[21] For most of the other compounds, energy refinements were obtained by single-point calculations with the 6-31G* basis at the 3-21G-optimized geometries. The effects of electron correlation were estimated by the use of second-order Møller–Plesset perturbation theory[22] (RMP2/6-31G*). Some geometrical details of **1–36** are summarized in Table I; complete specifications of all geometries (**Z** matrices and Cartesian coordinates) are available as supplementary material. Total energies are listed in Table II; total energies for some reference compounds, needed for the evaluation of reaction energies, have been collected in Table III. The procedures used for analyzing the electron density distribution $\rho(r)$ and its associated Laplace field $\nabla^2\rho(r)$ have been described before.[23,24] The analyses were carried out on HF/6-31G*//3-21G wave functions; the results are summarized in Tables VI and VII.

Part I. Geometries and Energies

1,3-Dioxetenes (1 and 4). The two choices of π-orbital occupations mentioned in the introduction lead to two completely different molecular geometries with comparable energies. The "aromatic" $\pi_1^2\pi_2^2\pi_3^2$ configuration produces a nearly square, planar molecule with a C–O bond length of 1.33 Å, close to that of the C–O single bond in vinyl alcohol (1.35 Å, both at 6-31G*;

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(16) Even if bicyclobutane would open in a concerted fashion, it would probably follow an asymmetric (C_1) path in which one of the rings opens conrotatorily and the other disrotatorily.[13-15] See also: Dewar, M. J. S. *Angew. Chem.* **1971**, *83*, 859. This is not necessarily true for the oxa- and azabicyclobutanes, where assistance by the O and N lone pairs is only possible in the symmetric paths. In any case, the difference between the two ring-opening modes disappears for dioxabicyclobutane.
(17) The GAUSSIAN 80 and GAUSSIAN 82 programs were used for all calculations. GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. GAUSSIAN 82: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, 1982. See also: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; Wiley: New York, 1986.
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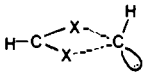
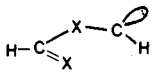
Table I. 3-21G (6-31G*) Geometry Data for **1–36** and Reference Compounds[a,b]

X	compd	C–X	∠XCX
O	**1**	1.369 (1.325)	90.9 (92.8)
NH	**9**	1.385	88.6



X	compd	C–X	C···X	∠CH,C···X$_2$
O	**2**	1.272 (1.244)	1.702 (1.584)	100.0 (103.8)
NH	**10**	1.323	1.542	114.2



X	compd	C=X	C(=X)–X	C(:)–X
O	**3**	1.189 (1.171)	1.397 (1.373)	1.359 (1.323)
NH	**12**	1.247	1.419	1.338

X	compd	C–C	C–X	α[c]
O	**4**	1.365 (1.338)	1.480 (1.419)	112.8 (113.9)
NH	**13**	1.410	1.521	108.2
	14	1.412	1.488,[d] 1.526	112.3
	15	1.420	1.494	120.6
	16	1.427	1.539, 1.441[e]	112.5
	17	1.430	1.505, 1.451[e]	117.7
CH_2	**32**	1.484	1.513	118.2

X	compd	C–C	C–X	C···X
O	**5**	1.366 (1.341)	1.351 (1.310)	1.700 (1.622)
NH	**18**	1.401	1.352	1.961
	20	1.410	1.344	1.823
CH_2	**33**	1.397	1.420	2.068

X	compd	C–C	C–X
O	**6**	1.504 (1.517)	1.206 (1.185)
NH	**21**	1.486	1.256
	22	1.482	1.256, 1.257
	23	1.475	1.257
	24	1.501	1.225,[e] 1.256.
	25	1.497	1.257, 1.228[e]
CH_2	**34**	1.467	1.320

X	compd	C–C	C–X	X–X	∠XCCX
O	**7**	1.350 (1.347)	1.355 (1.318)	1.779 (1.726)	16.8 (14.4)
NH	**26**	1.353	1.392	2.010	13.0
	27	1.360	1.397, 1.371	1.937	15.8
	28	1.368	1.373	1.920	21.8
CH_2	**35**	1.369	1.421	2.139	21.9

X	compd	C–C	C–X	X–X
O	**8**	1.310 (1.311)	1.443 (1.382)	1.502 (1.412)
NH	**29**	1.325	1.469	1.524
	30	1.326	1.469	1.523
	31	1.336	1.492, 1.405[e]	1.485
CH_2	**36**	1.326	1.539	1.593

molecule	X	C–C	C–X	X–X
CH_2=X	O		1.207 (1.184)	
	NH		1.256 (1.250)	
	(linear)		1.226 (1.220)	
	CH_2		1.315 (1.315)	
CH_3CH=X	O	1.507 (1.504)	1.209 (1.188)	
	NH	1.505 (1.505)	1.257 (1.252)	
	CH_2	1.510 (1.503)	1.315 (1.318)	
CH_2=CHXH	O	1.314 (1.318)	1.377 (1.347)	
	NH	1.324 (1.322)	1.378 (1.393)	
	CH_2	1.316 (1.318)	1.510 (1.503)	
CH_3XXH	O		1.445	1.469
	NH		1.469 (1.445)	1.446 (1.407)
	CH_2		1.541 (1.528)	1.541 (1.528)
$(CH_3)_2X$	O		1.433 (1.391)	
	NH		1.466 (1.447)	
	(planar)		1.444	
	CH_2		1.541 (1.528)	
CH_2CH_2X	O	1.474 (1.453)	1.470 (1.401)	
	NH	1.491 (1.471)	1.497 (1.449)	
	(planar)	1.544 (1.512)	1.418 (1.390)	
	CH_2	1.513 (1.498)	1.513 (1.498)	
CH=CHX	O	1.249 (1.244)	1.556 (1.467)	
	NH	1.264 (1.255)	1.560 (1.490)	
	(planar)	1.282 (1.271)	1.481 (1.446)	
	CH_2	1.282 (1.276)	1.523 (1.495)	

[a] For sources, see footnotes to Tables II and III. Complete specifications of the geometries are given as supplementary material. [b] Distances in Å, angles in deg. [c] Obtuse angle between the two CXC planes. [d] Distance to nitrogen atom of endo NH group. [e] Distance to nitrogen atom of inverting NH group.

see Table I). Clearly, the 6π-delocalization does not produce strong C–O π-bonds. The lack of stabilization in **1** is also evident from its high energy with respect to the open-chain isomer, glyoxal (**6**): the isomerization is exothermic by 75 kcal/mol! Diagonalizing the Hessian matrix results in one negative eigenvalue, demonstrating that **1** is not a local minimum. Relaxing the symmetry from D_{2h} to C_s results in a nonplanar $HCO_2^-\cdots CH^+$ complex **2**. This is still not a local minimum, although the single imaginary frequency is small (95*i* cm^{-1} at 3-21G) and the potential energy surface is very flat in this region. A barrierless ring opening finally produces planar (formyloxy)methylene **3** as the end product. A similar deformation of $C_4H_4^{2-}$ to a C_s structure with two long and two short C–C bonds was recently predicted by Hess and Schaad.[5] They did not, however, find any indication for an easy ring opening of this anion.

The alternative $\pi_1^2\pi_2^2\pi_4^2$ configuration produces the dioxabicyclobutane **4**. This species is somewhat higher in energy than **1**. Although the total energies at the equilibrium geometries of **1** and **4** are similar, both molecules are closed-shell species with a considerable HOMO–LUMO gap. The direct interconversion **1** $\rightleftharpoons$ **4** is symmetry-forbidden (the C–C σ-bond in **4** correlates

Figure 2. π-Complex representation of the bonding in three-membered-ring compounds.

with the empty π_4 in **1**) and cannot be described at the closed-shell RHF level. The large HOMO–LUMO gaps in both molecules and the large differences in geometries indicate that the isomerization reaction will have a considerable activation energy.

The structure of **4** shows a very short C–C bond (1.34 Å) more typical of a *double bond* than of a single bond. More modest compressions of C–C bonds in three-membered heterocycles are quite common and have also been observed in oxirane[25] and ox-

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Table II. Total and Relative Energies for **1–36**[a,e]

compd	E_{tot}, au			E_{rel}, kcal/mol		
	HF/3-21G[b]	HF/6-31G*	MP2/6-31G*	HF/3-21G	HF/6-31G*	MP2/6-31G*
			$(CHO)_2$			
1	−225.14229 (1)	−226.42582	−227.07852	103.3	104.4	75.4
2	−225.19268 (1)	−226.47013	−227.08483	71.7	76.6	71.4
3	−225.23492 (0)	−226.50835	−227.09938	45.2	52.6	62.3
4	−225.14712	−226.44322	−227.07195	100.3	93.5	79.5
5	−225.13296	−226.43349	−227.07573	109.2	99.6	77.1
6	−225.30696	−226.59218[c]	−227.19866	0	0	0
7	−225.13034	−226.38306	−227.04178	110.8	131.2	98.4
8	−225.17165	−226.42828[c]	−227.05851	84.9	102.8	87.9
			$(CHNH)_2$			
9	−185.75205 (1)	−186.78959	−187.41150	64.6	81.1	56.1
10	−185.76220 (0)	−186.80311	−187.40593	58.2	72.6	59.6
11	−185.74442 (1)	−186.78792	−187.36540	69.4	82.2	85.1
12	−185.80509	−186.85574	−187.42411	31.3	39.6	48.2
13	−185.70292	−186.78541	−187.39241	95.4	83.7	68.1
14	−185.72519	−186.80364	−187.40905	81.5	72.3	57.7
15	−185.73102	−186.81014	−187.41425	77.2	68.2	54.4
16	−185.67555	−186.74761	−187.35308	112.6	107.5	92.8
17	−185.69426	−186.76223	−187.36625	100.9	98.3	84.5
18	−185.62807 (2)	−186.71121	−187.34091	142.4	130.3	100.4
20	−185.67400 (1)	−186.74909	−187.36536	113.6	106.5	85.1
21	−185.85058	−186.91343	−187.49654	2.8	3.4	2.8
22	−185.85153	−186.91510	−187.49781	2.2	2.4	2.0
23	−185.85500	−186.91887	−187.50095	0	0	0
24	−185.81204	−186.86749	−187.45060	27.0	32.2	31.6
25	−185.81318	−186.86592	−187.44976	26.2	33.2	32.1
26	−185.71086 (1)	−186.76307	−187.38305	90.4	97.8	74.0
27	−185.71691 (1)	−186.76716	−187.38560	86.7	95.2	72.4
28	−185.72783 (1)	−186.77584	−187.39770	79.8	89.7	64.8
29	−185.77052	−186.82348	−187.42237	53.0	59.9	49.3
30	−185.78202	−186.83274	−187.43153	45.8	54.0	43.6
31	−185.76429	−186.81087	−187.40997	56.9	67.8	57.1
			$(CHCH_2)_2$			
32	−153.98664[d]	−154.86957	−155.40661	45.7	31.4	20.9
33	−153.82885	−154.70266	−155.25849	144.7	136.1	113.9
34	−154.05946[c]	−154.91961	−155.43995	0	0	0
35	−153.96436	−154.82459	−155.36847	59.7	59.6	44.9
36	−154.03072[c]	−154.89831	−155.42687	18.0	13.4	8.2

[a] The HF/6-31G* and MP2/6-31G* energies to 6-31G*-optimized geometries for **1–8** and to 3-21G-optimized geometries for **9–36**. [b] Number of imaginary frequencies given in parentheses. [c] From ref 47. [d] From ref 48. [e] We could not locate a stationary point corresponding to **19** (see text).

Table III. Total Energies (au) for Reference Compounds[a]

compd	HF/3-21G	HF/6-31G*	compd	HF/3-21G	HF/6-31G*
H_2O_2	−149.94582[c]	−150.76479[c]	N_2H_4	−110.55000[c]	−111.16937[c]
CH_3OH	−114.39802[c]	−115.03542[c]	CH_3NH_2	−94.68166[c]	−95.20983[c]
$(CH_3)_2O$	−153.21321[c]	−154.06474[c]	$(CH_3)_2NH$	−133.49485[c]	−134.23885[c]
CH_3OOH	−188.76311	−189.79143[b]	(planar)	−133.49066	−134.22954[b]
CH_3CH_2OH	−153.22292[c]	−154.07574[c]	CH_3NHNH_2	−149.36509	−150.20108[c]
CH_2=$CHOH$	−152.04176[c]	−152.88888[c]	$CH_3CH_2NH_2$	−133.50415[c]	−134.24761[c]
CH_2=O	−113.22182[c]	−113.86633[c]	CH_2=$CHNH_2$	−132.32644[c]	−133.06196[f]
CH_3CH=O	−152.05525[c]	−152.91596[c]	(planar)	−132.32644[f]	−133.05920[f]
CH_2CH_2O	−152.00070[c]	−152.86736[e]	CH_2=NH	−93.49478[c]	−94.02846[c]
CH=CHO	−150.72861[d]	−151.58390	(linear)	−93.45319[c]	−93.97672[c]
CH_2CH_2OO	−226.37886		CH_3CH=NH	−132.32300[c]	−133.07384[c]
CH_2OCH_2O	−226.45374	−227.73111	CH_2CH_2NH	−132.27801[c]	−133.03855[e]
:$CHCH$=O	−150.74160[c]	−151.60768[c]	(planar)	−132.25731	−133.00765[c]
CH_3CH_3	−78.79395[c]	−79.22875[c]	CH=$CHNH$	−131.01750[d]	−131.77555[c]
$CH_3CH_2CH_3$	−117.61330[c]	−118.26365[c]	(planar)	−130.95370	−131.70288[c]
CH_2=CH_2	−77.60099[c]	−78.03172[c]	CH_2CH_2NHNH	−186.98252	
CH_3CH=CH_2	−116.42401[c]	−117.07147[c]	CH_2NHCH_2NH	−187.00421	
$CH_2CH_2CH_2$	−116.40121[c]	−117.05887[c]	:$CHCH$=NH	−131.01107	
CH=$CHCH_2$	−115.16201[c]	−115.82305[c]			
$CH_2CH_2CH_2CH_2$	−155.23137	−156.09703[g]			

[a] HF/6-31G*//6-31G* energies unless otherwise noted. [b] HF/6-31G*//3-21G. [c] From ref 47. [d] From ref 26. [e] From ref 25. [f] From ref 49. [g] From ref 50.

irene[26,27] (cf. Table I). They are most easily explained by describing such rings as π-complexes.[25,28] Cyclopropene can be considered as a complex between ethylene (σ-donor, π-acceptor) and π^2-singlet methylene (π-donor, σ-acceptor) as illustrated in

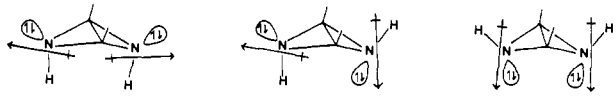
Figure 2. The larger electronegativity of oxygen, compared to carbon, results in a larger ethylene→O σ-donation and a smaller O→ethylene π-back-donation. Thus, oxirane can be considered as an ethylene–oxygen π-complex; similarly, oxirene and **4** can be described as complexes of acetylene with one or two oxygen atoms, respectively.

1,2-Dioxetene (8). In this 1,2-substituted 6π-system, the π-orbitals π_3 and π_4 belong to the same irreducible representation of the C_{2v} point group (Figure 1b). The large electronegativity of oxygen causes them to mix in such a way as to maximize the coefficients on oxygen. This results in a classical cyclic peroxide structure for 1,2-dioxetene. The bond lengths in the four-membered ring do not show any effects of 6π-delocalization (C–O = 1.38 Å at 6-31G*; cf. 1.35 Å in vinyl alcohol (see Table 1)), and the high energy with respect to glyoxal clearly shows the lack of aromatic stabilization.

1,3-Diazetines (9 and 13–15). The structural types that were found in the dioxetene series are also possible for the diazetines, but the presence of hydrogen atoms on nitrogen results in a larger number of isomers. The "aromatic" $\pi_1^2\pi_2^2\pi_3^2$ D_{2h} structure of 1,3-diazetine is found to be a nearly square molecule (**9**) with a C–N bond length of 1.39 Å (at 3-21G), comparable to that in vinylamine (1.38 Å at 3-21G; see Table I). Like **1**, **9** is not a local minimum at the RHF/3-21G level.[29] When the symmetry is lowered, further optimization gives the nonplanar C_s HC(NH)$_2^-$···CH$^+$ complex **10**, which is a local minimum at RHF/3-21G. Ring opening (via **11**) finally produces formimidinomethylene **12** (which is calculated to be 8 kcal/mol *more stable* than **9**) with an activation energy of 25 kcal/mol (at MP2/6-31G*//3-21G). Minyaev and Minkin, who studied **9** at the MINDO/3 level, found it to have a structure with C_i symmetry and an energy *below* that of **12**, **15**, and **30**.[6] Our MP2/6-31G* results are expected to be more reliable.

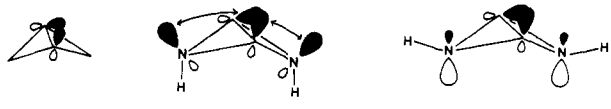
In contrast to the oxygen series, the "aromatic" 1,3-diazetine **9** is slightly higher in energy than its most stable bicyclobutane-like isomer **15**. The diazabicyclobutanes **13–15** are highly strained systems, though less so than their oxygen analogue **4**. The bridgehead C–C bonds are much longer than those in **4**: the diazabicyclobutanes bear little resemblance to acetylene–NH π-complexes. A similar lack of π-complex character is observed in aziridine[25] and azirine.

The energy ordering **13** > **14** > **15** may be caused by the more favorable bond dipole arrangements in the endo-NH compounds: the total dipole moments (3-21G) are 4.96 (**13**), 2.73 (**14**), and 0.81 D (**15**). Another contribution may come from participation



15 14 13

of the exo nitrogen lone-pair orbitals (two in **15** and one in **14**) in the bridgehead-bonding orbital. As a consequence, the C–N bonds are strengthened relative to those in **13** (1.494 vs 1.521 Å; see Table I) while the C–C bond is weakened (1.420 vs 1.410 Å). The former effect prevails, and **15** is more stable than **13** where lone-pair participation in C–N bonding is small for geometrical reasons:



32 15 13

The decrease of the obtuse angle α between the two CNC planes in the order **15** > **14** > **13** (Table I) also supports this interpretation; apparently, nitrogen lone-pair participation dominates over lone pair–lone pair repulsions, which would favor the opposite ordering.

A point of interest is the barrier for inversion at nitrogen. The small inversion barrier calculated for dimethylamine (6 kcal/mol at 6-31G*) is raised considerably when the CNC valence angle is decreased on going to aziridine (ca. 20 kcal/mol; see Table IV). The smaller valence angle at N results in decreasing s character of the C–N bonds and increasing s character of the nitrogen lone pair. Therefore, the energy required to reach the transition state for inversion, in which the s character of the lone pair vanishes, becomes larger.[30] The inversion barriers of the diazabicyclobutanes are even larger than that in aziridine (by 10 kcal/mol). However, they remain much lower than the 46 kcal/mol calculated for azirine where the planar transition state is strongly destabilized by antiaromatic 4π-interactions.

1,2-Diazetines (29 and 30). As in the oxygen series, no indications of 6π-aromaticity are found for the 1,2-diazetines. The nitrogen atoms are pyramidal, and the N–N (1.52 Å) and C–N (1.47 Å) bond lengths are much longer than those in the reference compounds methylhydrazine (N–N = 1.45 Å) and vinylamine (C–N = 1.38 Å), respectively (see Table I); the C=C bond is a normal double bond (1.33 Å). The calculated average nitrogen inversion barrier in 1,2-diazetine (11 kcal/mol at 6-31G*) is much lower than those in **13–15** but appreciably higher than that of vinylamine or even dimethylamine calculated at the same level (HF/3-21G underestimates these barriers; see Table IV). Thus, the possibility of increased delocalization in the transition state does not lead to a substantial lowering of the inversion barrier. Actually, the noninverting nitrogen atom slightly *increases* its pyramidalization as the other nitrogen atom inverts. The completely planar C_{2v} structure of 1,2-diazetine is calculated to be 21 kcal/mol less stable than **29**. This behavior contrasts with that of the 6π five-membered-ring heterocycle pyrrole, which has a planar NH group.[31] Minyaev and Minkin apparently did not consider the possibility that 1,2-diazetine might be nonplanar; this may be the reason that they found it to be higher in energy than **9**. Our calculations indicate that **30** is the lowest energy *cyclic* $(CHNH)_2$ isomer.

Conrotatory Ring Opening of Cyclobutene, 1,2-Diazetine, and 1,2-Dioxetene. The conrotatory ring opening of cyclobutene has been studied in detail at the ab initio TCSCF/CI level by Schaefer et al.[12] For comparison with the nitrogen and oxygen systems, we have reoptimized the transition state at the RHF/3-21G level. Inspection of Table II shows that the activation energy decreases by ca. 15 kcal/mol on going from cyclobutene to its diaza analogue. This energy lowering is undoubtedly caused by the weakness of the N–N bond compared to the C–C bond. The decrease in activation energy is observed for the paths via **27** and

Table IV. Inversion Barriers (kcal/mol)[a]

molecule	HF/3-21G	HF/6-31G*
$(CH_3)_2NH$	2.6	5.8
CH_2=$CHNH_2$	0	1.7
CH_2CH_2NH	13.0	19.4[c]
CH=CHNH	40.0	45.6
13–15[b]	22.9	28.8
29, **30**[b]	5.6	10.9
CH_2=NH	26.1	32.5
21–23[b]	24.8	30.7

[a] Calculated from the data in Tables II and III. [b] Averages of all possible forward and backward activation energies. [c] The MP2/6-31G*//6-31G* and experimental values are 19.9 and 19.0 kcal/mol, respectively.[51]

(26) Carsky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 396.
(27) Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869.
(28) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.
(29) At MP2/6-31G*//3-21G, the energy of **9** is slightly lower than that of **10**. This might mean that **9** is a minimum at higher levels of theory or that the true minimum is somewhere between **9** and **10**.
(30) See, e.g.: Lehn, J. M. *Top. Curr. Chem.* **1970**, *15*, 311. Malpass, J. R. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D. Eds.; Pergamon: New York, 1979; Vol. 2, pp 26ff.
(31) Wilcox, W. S.; Goldstein, J. H. *J. Chem. Phys.* **1952**, *20*, 1656. Nygaard, L.; Neilsen, J. T.; Kirchheiner, J.; Maltesen, G.; Rastrup-Andersen, J.; Sørensen, G. O. *J. Mol. Struct.* **1969**, *3*, 491.

Table V. Reaction Energies (kcal/mol)[a]

X	1	2	3	4	5	6	7	8	9	10	11	12
						RHF/3-21G						
O	−24.7	−38.8	−0.3	−24.2	−20.9	+5.3	−31.4	+38.1	−4.3	−4.1	−14.8	−14.6
NH	−11.8	−17.9	−3.0	−5.8	−16.4	+7.3	−30.9	+50.0	+2.4	+0.1	−12.2	−14.6
						RHF/6-31G*						
O	−17.9	−37.9	+4.6	−27.2	−25.3	+3.3	−31.9	+46.0	+6.6	*b*	−0.1	*b*
NH	−6.2	*b*	+2.8	−11.8	−14.2	+4.1	−22.4	+38.7	+0.1	*b*	−8.1	*b*

[a] Calculated from the data in Tables II and III. [b] The necessary 6-31G* energies for the reference compounds are not available.

28, where the nitrogen lone pairs move to avoid one another, but is much less for **26**, where they move toward one another. Apparently, the increased lone pair–lone pair repulsion costs ca. 10 kcal/mol in **26**. The ring opening of 1,2-dioxetene is calculated to be even more facile, with an activation energy of ca. 11 kcal/mol.

Ring-Opening Reactions of Bicyclobutane Analogues. Although the stereochemistry of the ring opening of bicyclobutane to butadiene agrees with that predicted by the Evans principle[15,16] or from the Woodward–Hoffmann rules[14] for a concerted mechanism, MNDO calculations by Dewar strongly suggested that the reaction is actually a two-step process involving a biradicaloid intermediate.[15] For comparison with the nitrogen and oxygen systems, we have optimized the "transition structure" **33** for the C_2-symmetrical concerted ring-opening reaction at the RHF/3-21G level. The energy of **33** was found to be 93 kcal/mol higher than that of bicyclobutane **32**, which excludes a C_2 concerted mechanism,[16] in agreement with the results of Closs and Pfeffer.[14] This is not very surprising. In order to form the new π-bonds, the methylene bridges must rotate by ca. 90° around two CH–CH_2 single bonds; this is only possible *after* the other two CH–CH_2 bonds have been broken (Figure 3A). It must be better for *one* σ-bond to break first; the resulting biradical can then reorient in such a way that the rupture of the second C–C σ-bond is compensated by the simultaneous formation of a new π-bond. However, our computational results do not exclude an *asymmetric* (conrotatory, disrotatory) concerted ring opening.[13,14]

The activation energy for the C_2-symmetric concerted ring-opening reaction of diazabicyclobutane **15** is much smaller, only 31 kcal/mol. Here, the symmetric mechanism cannot immediately be discounted. The lower activation energy is not caused primarily by lower C–N bond strengths. A more important factor is the fact that in these heterosubstituted compounds σ-bond breaking does not have to be complete before π-bond formation begins. Instead of transforming two σ-bonds to two π-bonds, as in bicyclobutane, the two σ-bonds are converted into two nitrogen lone pairs; meanwhile, the original lone pairs transform into C–N π-bonds (Figure 3B).

Scheme II shows the ring-opening reactions of the three isomeric diazabicyclobutanes **13–15** leading to the three α-diimines **21–23** via the transition states **18–20**. Actually, this is somewhat misleading. The stationary point **18** for the reaction **13** → **21** has two imaginary frequencies; one corresponds to the ring-opening reaction, the other to inversion at *one* of the nitrogen atoms. Thus, **13** inverts at nitrogen to give **14** before opening. Searches in the neighborhood of the hypothetical transition state **19** for the reaction **14** → **22** did not even reveal a stationary point of higher order. Apparently, the *second* nitrogen atom also inverts (to give **15**) before ring-opening occurs. The most stable diazabicyclobutane **15** finally opens to **23** with an activation energy of 31 kcal/mol.

The activation energy for symmetric opening of **4** is even lower than that for **15**. Actually, when the 3-21G-optimized transition structure (**5**) is used for a MP2/6-31G* single-point calculation, the resulting energy is *lower* than that of **4**. This suggests that the opening of **4** is barrierless. Figure 3C illustrates the orbital changes accompanying the formation of glyoxal from **4**. Again, an interchange of bonding and lone-pair orbitals is observed during the reaction.

The large influence of heteroatom substitution on the ring opening of *bicyclobutanes* should be contrasted with the much smaller effects calculated for the *cyclobutene* derivatives (vide supra). In the reactions of the latter species, no interchange of σ-bonding and lone-pair orbitals occurs, and the concerted mechanism observed for the parent cyclobutene is not changed fundamentally by the introduction of the heteroatoms.

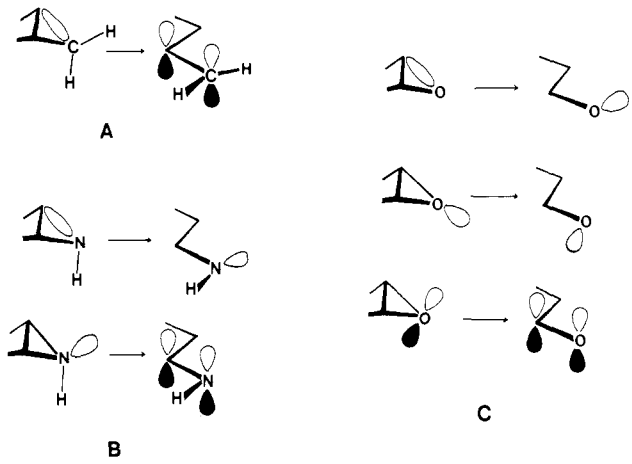
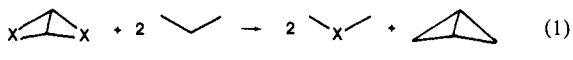
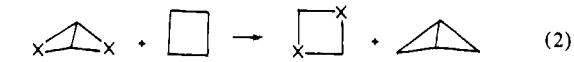


Figure 3. Schematic representation of the orbital changes accompanying the ring-opening reactions of **32** (A), **15** (B), and 4 (C) in a concerted (C_2) mechanism.

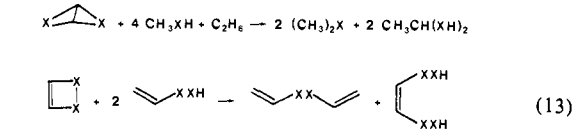
Ring Strain in Bicyclobutane Derivatives. The ring strain energies of the bicyclobutane derivatives were estimated from reactions 1 and 2:[32]


(1)

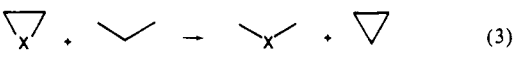

(2)

The data in Table V show that the oxa- and azabicyclobutanes are significantly more strained than the parent hydrocarbon. In contrast, the simple three-membered-ring compounds oxirane and aziridine have approximately the same ring strain as cyclopropane, as calculated from homodesmotic separation energies[32] or from eq 3 (see Table V):

(32) The best way to evaluate strain energies is the use of homodesmotic reactions. This procedure has been described in detail by Bock et al. for carbocyclic compounds (George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans 2* **1977**, 1036). Although the extension to heteroatom-substituted systems poses no fundamental problems, it often leads to unwieldy equations involving complicated reference compounds; e.g.

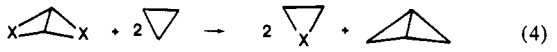

(13)

Therefore, we decided to use isodesmic reactions to relate the strain energies of the oxa and aza systems to those of the parent hydrocarbons. However, these isodesmic reactions contain some contributions from other factors than ring strain (e.g., C–X, C–X bond separation energies: Schleyer, P. v. R.; Kos, A. J. *Tetrahedron Lett.* **1983**, *39*, 1141).



(3)

The strain energy of bicyclobutane is larger than that of two cyclopropanes;[33] this "strain excess" can be explained from the analysis of the electron density distribution (vide infra). The "strain excess" of **4** and **15** is even larger, as illustrated by the exothermicity of eq 4:

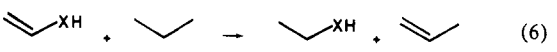


(4)

Bicyclobutanes as π-Complexes. If one considers bicyclobutanes as π-complexes, a comparison with the substituted cyclopropenes is appropriate. The "strain energies" of oxirene and azirine are compared with that of cyclopropene in eq 5:

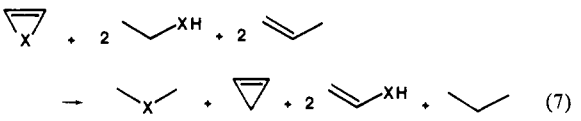
(5)

The comparison is not quite fair, however, since C(sp^2)–X bonds are stronger than C(sp^3)–X bonds, as calculated from eq 6:



(6)

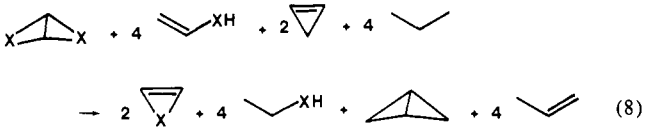
Correction for this hybridization effect (eq 7) produces a destabilization energy of 32 kcal/mol for oxirene and 22 kcal/mol for azirine:



(7)

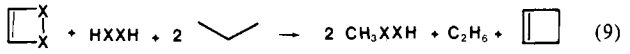
Both oxirene and azirine are 4π-systems, and the destabilization energy can largely be attributed to antiaromaticity. This antiaromatic destabilization might be expected to be greater for azirine, where the C–X electronegativity difference, which determines the deviation from the truly antiaromatic cyclopropenyl anion,[34] is smallest. However, azirine avoids the destabilizing 4π-repulsion by becoming highly nonplanar; using only planar nitrogen molecules in the evaluation of eq 7, one obtains a destabilization energy of ca. 70 kcal/mol!

According to the π-complex formalism, formation of a three-membered ring decreases the π-character of the original π-bond. Complexation with a second X atom will thus decrease the π-character of the second π-bond and diminish the unfavorable 4π-repulsions. Accordingly, the energies calculated for eq 8 (the combination of eq 1 and 7) are strongly endothermic, 46 kcal/mol for X = O and 39 kcal/mol for X = NH.

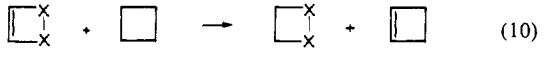


(8)

Ring Strain in Cyclobutene Derivatives. The ring strain of the cyclobutene derivatives **8** and **29** is compared with that of the parent **36** in eq 9 and 10:

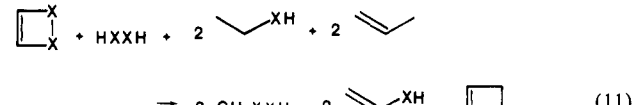


(9)

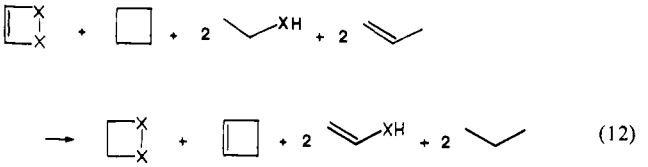


(10)

As in the previous section, this equation has to be corrected for the changes in the types of C–X bonds; subtracting 2 × (eq 6) gives eq 11 and 12:



(11)



(12)

The exothermicity of these reactions shows that the oxa- and azacyclobutenes are slightly more strained than their carbon counterpart. This may be partly due to the unfavorable conformations around the X–X bonds in **8** and **29**. In any case, there is no evidence for a stabilizing 6π-interaction, which would make these reactions endothermic.

Part II. Electron Density Analyses

General Aspects. In order to get a better insight into the structural and bonding features of the dioxetenes and diazetines, we have investigated the calculated total electron density distribution $\rho(r)$ and its associated Laplace field $\nabla^2\rho(r)$ of these compounds, as well as some appropriate reference molecules, along the lines developed earlier.[23,24] Of interest are the properties of $\rho(r)$ in the bonding region, in particular at the bond path and at the bond critical point r_b. The bond path corresponds to the path of maximum electron density linking two bonded atoms. It is an image of the bond. The network of bond paths in a molecule leads to the molecular structure.

The minimum of $\rho(r)$ along the bond path, ρ_b, defines the position r_b of the bond critical point. It is a saddle point of $\rho(r)$ in three dimensions. The value of ρ_b can be used to determine the bond order n.[23,24] The bond critical point is not necessarily positioned on the internuclear axis. In the case of a bent bond, r_b is shifted by a distance d from the internuclear axis. The magnitude of d is a measure of the bent-bond character of a bond.[24,25]

Three-Membered Rings and π-Complexes. Cremer and Kraka have shown that in the case of three-membered rings bond paths may be convex or concave; i.e., they may be curved outwardly or inwardly with regard to the center of the ring.[25] Convex bond paths lead to interpath angles β that are larger than geometrical angles α while concave bond paths imply $\beta < \alpha$. A continuous decrease of β describes the structural change of a three-membered ring to a π-complex with a T structure. Such a change is observed if in compounds AXA the electronegativity of the atom or group X interacting with the basal group A_2 increases.[25] It can be rationalized by considering AXA as a donor–acceptor complex.[25,28] In the three-membered ring, X (or A_2) acts as a σ-acceptor and a π-donor with regard to A_2 (or X), with the π-donor ability prevailing. With increasing electronegativity of X (A_2), the σ-acceptor ability becomes dominant and a π-complex results.[25,28]

Changes in the electronic structure of a three-membered ring can also be assessed by an investigation of the Laplace field $\nabla^2\rho(r)$.[35,36] The Lapacian of $\rho(r)$ indicates whether negative charge is concentrated ($\nabla^2\rho(r) < 0$) or depleted ($\nabla^2\rho(r) > 0$). Concentration lumps in a molecule can be assigned to inner-shell electrons, bond electron pairs, and electron lone pairs.[35,36]

Bonding in the Planar Dioxetenes and Diazetines. In Table VI, calculated HF/6-31G* values of ρ_b, bond orders n, and distances d are listed for *trans*-butadiene, cyclobutene, bicyclobutane, and their diaza and dioxa analogues. Bond orders n larger than 1 are indicative of (partial) double-bond character. Accordingly, the bond orders calculated for **6**, **23**, and **34** are typical of an acyclic system with two conjugated double bonds. Due to π-delocalization, the formally single C–C bond acquires 25–30% π-character.

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Table VI. Bond Orders n and Bent-Bond Characters d As Determined by the Properties of $\rho(r)$[a]

X	compd	bond	ρ_b, e Å^{-3}	n[b]	d, Å
O	**6**	C=X	2.78	2.08	0
NH	**23**		2.70	2.11	0.01
CH_2	**34**		2.45	1.95	0
O	**6**	C–C	1.92	1.25	0
NH	**23**		1.97	1.30	0
CH_2	**34**		1.92	1.25	0
O	**1**	C–X	1.86	1.12	0
NH	**9**		1.98	1.18	0.03
O	**8**	C=C	2.53	2.10	0.04
NH	**30**		2.45	1.95	0.04
CH_2	**36**		2.44	1.94	0.04
O	**8**	C–X	1.67	0.99	0
NH	**30**		1.84	1.05	0.03
CH_2	**36**		1.67	1.01	0.05
O	**8**	X–X	1.75		0
NH	**30**		1.78		0.02
CH_2	**36**		1.53		0.04
O	HXXH[c]	X–X	2.25	1.00	0
NH			2.19	1.00	0
CH_2			1.71	1.00	0
O	**4**	C–C	2.16	1.53	0.12
NH	**15**		1.88	1.21	0.11
CH_2	**32**		1.62	0.96	0.09
O	**4**	C–X	1.62	0.96	−0.02
NH	**15**		1.70	0.94	0.03
CH_2	**32**		1.64	1.01	0.06
O	[d]	C–C	1.82	1.12	0.09
NH			1.76	1.06	0.08
CH_2			1.68	0.98	0.06
O		C–X	1.77	1.00	0.00
NH			1.82	0.97	0.04
CH_2			1.68	0.98	0.06

[a] HF/6-31G* calculations at 3-21G geometries. [b] $n = \exp[a(\rho_b - b)]$; see ref 24. [c] From ref 24. [d] From ref 25.

Table VII. Comparison of Interpath Angles β[a] and Geometrical Angles α[b]

X	compd	α_{CXC}	β_{CXC}	α_{CCX}	β_{CCX}	α_{XCX}	β_{XCX}
O	**4**	54.9	67.2	62.5	62.4	95.3	83.0
NH	**15**	56.7	67.5	61.6	73.9	99.7	96.4
CH_2	**32**	58.7	73.6	60.6	77.4	96.8	103.7
O	[c]	62.4	75.8	58.8	72.8		
NH		60.9	76.4	59.5	77.3		
CH_2		60.0	78.8	60.0	78.8		

[a] HF/6-31G* calculations. [b] HF/3-21G geometries for **4**, **15**, and **32**; HF/6-31G* geometries for cyclopropane, aziridine, and oxirane. [c] From ref 25.

In the 6π-systems **1** and **9**, the double-bond character of the C–N and C–O bonds is reduced to 18 and 12%. π-Delocalization is suppressed relative to acyclic reference compounds. It vanishes completely in the case of 1,2-diaza- and 1,2-dioxacyclobutene. The C–X bonds of these molecules possess bond orders close to 1, while n(C=C) is close to 2 (Table VI). The ρ_b values of the X–X bonds in **36** (X = CH_2), **30** (X = NH), and **8** (X = O) reveal that this bond is weakened: ρ_b(X–X) is 11, 19, and 22% smaller than the corresponding value in C_2H_6, N_2H_4, and H_2O_2, respectively.[24] This is in line with the calculated relative stabilities of **36**, **30**, and **8**.

Bonding in Bicyclobutane Analogues. A comparison of the bond orders obtained for bicyclobutane (**32**), diazabicyclobutane (**15**), and dioxabicyclobutane (**4**) (Table VI) in conjunction with an analysis of the calculated interpath angles β shown in Table VII leads to some interesting observations:

(1) When going from bicyclobutane to diaza- and then to dioxabicyclobutane, there is a dramatic increase in the bridgehead C–C bond order, from 1 to 1.5. Thus, the C–C bond in **4** possesses 50% double-bond character due to the reduced back-donation from O to C–C (vide infra).

(2) At the same time, the C–X bond orders decrease. The C–O bonds of **4** should be weaker than those of oxirane (Table VI).

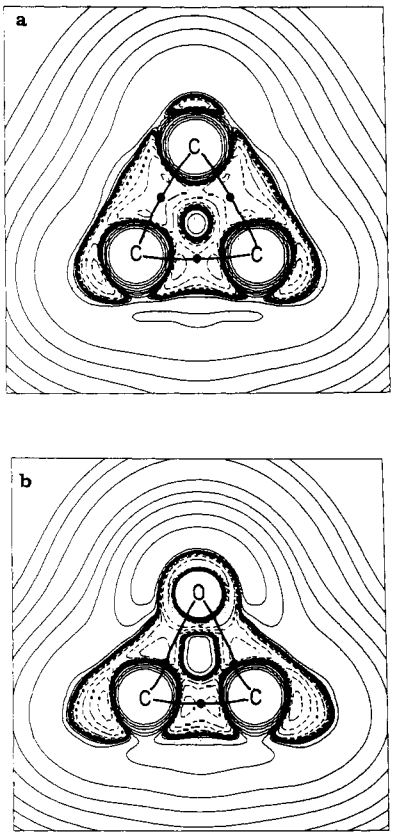

Figure 4. Molecular graphs and contour diagrams of the Laplace concentration $\nabla^2\rho(r)$ of (a) bicyclobutane and (b) dioxabicyclobutane in the plane of one of the three-membered rings. Dashed contour lines are in regions where electronic charge is concentrated ($\nabla^2\rho(r) < 0$) and solid lines are in regions where charge is depleted ($\nabla^2\rho(r) > 0$). Note that charge concentrations in the inner-shell regions are not shown. Bond paths are indicated by heavy lines, and bond critical points by dots. In those cases where the bond path leaves the reference plane its projection is shown; the strong curvature of the central C–C bond is poorly illustrated by this projection.

(3) According to the calculated d values, the bend of the bridgehead C–C bond is significantly larger than that of the C–C bonds in cyclopropane, aziridine, and oxirane (Table VI). In all these molecules, the C–C bond paths are convex.

(4) The interpath angles β (Table VII) of the bicyclic systems **4**, **15**, and **32** are smaller than those of the corresponding three-membered rings. The deviations increase in the series X = CH_2, NH, O. Accordingly, angle strain (Bayer strain) in bicyclobutane **32** should be larger than twice the strain calculated for cyclopropane.[37] Furthermore, angle strain should increase when replacing the CH_2 groups in **32** by NH or O. Both predictions are in line with the reaction energies given in Table V (reactions 1 and 2).

In Figure 4 contour diagrams of the calculated Laplace concentrations of bicyclobutane and dioxabicyclobutane (in the heavy-atom plane of one of the two three-membered rings) are shown. The qualitative features of the Laplace concentrations of **32** and **4** are similar to those found for cyclopropane and oxirane.[25] The same holds for the bond paths (given by the heavy solid lines in Figure 4) and the positions of the bond critical points (dots in Figure 4) in bicyclobutane. However, in the case of dioxabicyclobutane the C–O bond paths are slightly curved inwardly (concave) rather than outwardly (convex) as found for oxirane.[25] The bending of the C–N bond paths of diazabicyclobutane is intermediate: the bonds are convex but the bending is less pronounced than in aziridine.

π-Complex Character of Bicyclobutane and Cyclopropene Analogues. In order to get a better understanding of these ob-

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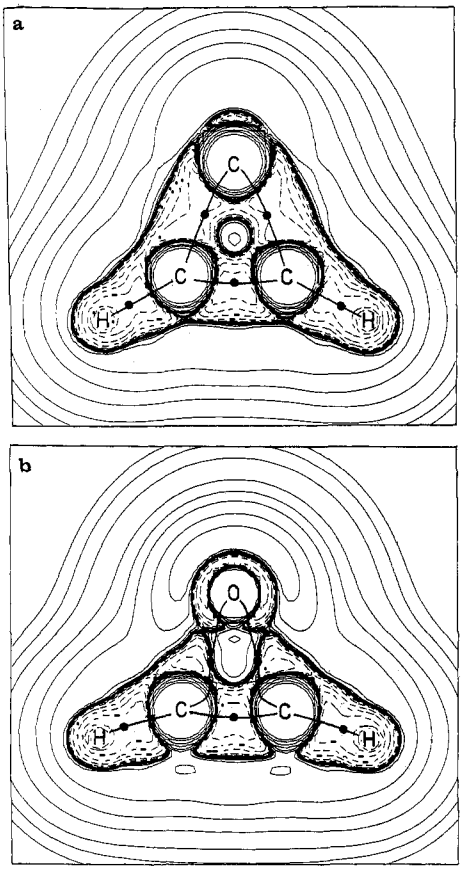

Figure 5. Molecular graphs and contour diagrams of the Laplace concentrations $\nabla^2\rho(r)$ of (a) cyclopropene and (b) oxirene. For explanation, see Figure 4.

servations, we have also investigated the bent bonds of cyclopropene, azirine, and oxirene. Contour diagrams of $\nabla^2\rho(r)$, bent bonds, and bond critical points of cyclopropene and oxirene are shown in Figure 5. The figure reveals that the increase in concave bending with increasing electronegativity of X is much more pronounced in the unsaturated three-membered rings than in the saturated ones. The bend of the CO bonds resembles that found for protonated oxirane (see Figure 1 of ref 25), a molecule that is structurally close to a π-complex between ethylene and OH^+.[25] Similarly, the structure of oxirene can be considered to be close to that of a π-complex between acetylene and oxygen. As a consequence the C–O bonds are labile and the stability of oxirene is considerably reduced.[38] The relatively high π-complex character of oxirene is easily explained on the basis of donor–acceptor interactions between O and acetylene.[25,28] If O would act just as a σ-acceptor, accepting negative charge from the π MO of acetylene, the T structure of a π-complex would result. π-Back-donation into the π^* MO of acetylene leads to a buildup of electron density in the CO internuclear region (see Figure 3 of ref 25). A three-membered ring with concave (weak π-back-donation) or convex bonds (strong π-back-donation) is formed. Since the π^* MOs of acetylene are higher in energy than the π^* MO of ethylene, acetylene is a weaker π-acceptor than ethylene and π-back-donation from O is small. As a consequence, oxirene is a labile three-membered ring closely related to an oxygen–acetylene π-complex.

In the case of dioxabicyclobutane, donor–acceptor interactions between acetylene and *two* O atoms have to be considered. Acetylene donates electrons to both O atoms and, therefore, loses more charge than in the oxirene case. To compensate this loss, π-back-donation is stronger and the C–O bonds are more developed (less concave) than in oxirene. Hence, dioxabicyclobutane takes an intermediate position between oxirane and oxirene. Its π-complex character is stronger and its stability is considerably lower than that of oxirane.

Similar conclusions can be drawn when comparing aziridine, diazabicyclobutane, and 2-azirine. These results are in line with the reaction energies summarized in Table V (reactions 7 and 8).

Part III. Stabilities with respect to Open-Chain Isomers

One remarkable aspect of the heterocycles studied here is their high energy relative to the open-chain species, glyoxal (**6**) and α-diimine (**23**). Both **4** and **8** are more than 75 kcal/mol higher in energy than **6**! The situation is somewhat less extreme for the nitrogen compounds, but the ring-opening reactions of both **15** and **29** are still highly exothermic (by over 50 kcal/mol). The corresponding conversions of bicyclobutane (**32**) and cyclobutene (**36**) to butadiene (**34**) are much less exothermic, by only 21 and 8 kcal/mol, respectively. The results discussed in the previous sections indicate that the heteroatoms cause only modest increases in ring strain. A more important contribution comes from the increasing strength of the C=X double bond in the sequence C < N < O and the decreasing strength of the X–X bond in the same order. This trend results in a stabilization of the open-chain compounds (which have two C=X double bonds) and a destabilization of the cyclobutene derivatives (which have one X–X bond).

The high exothermicities of all ring-opening reactions lead one to wonder whether dioxetenes or diazetines can exist as stable chemical species. In analogy with the 1,2-dioxetane syntheses,[39] the most obvious route to 1,2-dioxetenes would be the reaction of singlet oxygen with acetylenes. Indeed, Turro et al. have observed an intermediate in the reaction of 5-thiacycloheptyne with singlet oxygen, which decomposed above −30 °C to the corresponding 1,2-dione with emission of light. A dioxetene structure was proposed for this intermediate,[40] and the activation energy for its decomposition (18 kcal/mol) is compatible with our computational results. Turro did not observe any reactions with less strained acetylenes.

Two 1,2-diazetines have been reported from the reaction of bis(2,6-dimethyl-4-methoxyphenyl)acetylene with triazolinediones.[9] The latter reagents are diimide derivatives, which undergo several reactions reminiscent of those of singlet oxygen.[9] Hence, the formation of diazetine derivatives with acetylenes is not very surprising. A rather unstable 1,2-diazetine was obtained by Nunn; its ^{1}H NMR spectrum indicated the absence of a significant ring current.[10] Effenberger prepared some "push-pull"-substituted derivatives, which appear to be more stable.[10]

In view of the barrierless opening of **4** to **6**, preparation of acetylene diepoxides seems unlikely, although these compounds have been suggested as intermediates in the peroxidation of acetylenes.[41] The nitrogen analogues **13–15** should be somewhat more stable, and a few derivatives have been reported.[42] The monoazabicyclobutanes prepared to data all have the nitrogen atom at the bridgehead position;[43] 2-oxa- and 2-azabicyclobutanes have been postulated as unstable intermediates.[44,45] Derivatives of the planar 1,3-dioxetene **1** are predicted to be unstable and undergo barrierless opening to (formyloxy)carbenes.[46] 1,3-

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Diazetines (**9**) might not open as easily, but are expected to be highly reactive.

Conclusions

The lack of aromaticity of four-membered-ring 6π-heterocycles can be attributed to two main factors, viz., the strongly 1,2- and/or 1,3-antibonding character of the higher occupied π-orbitals and the electronegativity difference between C and O or C and N. Both factors favor localization of π-electrons and ring-opening reactions. Presumably, 6π-aromaticity requires at least a five-membered-ring system, where the nonbonded repulsions are much less severe.

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Registry No. 1, 287-50-3; **3**, 110175-39-8; **4**, 110175-40-1; **6**, 107-22-2; **8**, 287-35-4; **9**, 5663-08-1; **12**, 74726-45-7; **13**, 27670-35-5; **21**, 40079-19-4; **29**, 13473-83-1; **32**, 157-33-5; **34**, 106-99-0; **36**, 822-35-5; $(CH_3)_2NH$, 124-40-3; $CH_2{=}CHNH_2$, 593-67-9; CH_2CH_2NH, 151-56-4; CH=CHNH, 157-17-5; $CH_2{=}NH$, 2053-29-4.

Supplementary Material Available: Complete specifications (**Z** matrices and Cartesian coordinates) of the geometries of **1–36** (10 pages). Ordering information is given on any current masthead page.

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Theoretical Modelling of Specific Solvation Effects upon Carbonyl Addition

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Abstract: Geometries have been fully optimized at the HF/3-21G and AM1 levels of theory for reagent, activated, and product complexes for ammonia addition to formaldehyde catalyzed by 0, 1, or 2 molecules of water. One water molecule reduces the 3-21G reaction barrier by 113 kJ mol^{-1} by virtue of increased hydrogen bonding with the zwitterion-like ammonia–formaldehyde moiety in the cyclic six-membered activated complex. The second water molecule reduces the barrier by a further 33 kJ mol^{-1} in 3-21G by permitting less-bent hydrogen bonds in the cyclic eight-membered activated complex. Hydrogen bond strengths are overestimated at the 3-21G and MP2/6-31G*//3-21G levels but are underestimated by AM1, particularly for hydrogen bonds involving charged species; AM1 consistently prefers bifurcated to linear hydrogen bonds. Relative Gibbs free energies of activation estimated for the addition reactions predict the two-water-catalyzed process to be preferred over the one-water-catalyzed process by ~10 kJ mol^{-1} in the gaseous and aqueous phases and by ~25 kJ mol^{-1} in dioxan. The reaction-coordinate vibrational modes are dominated by motions of the transferring protons; proton donation is more advanced than proton abstraction in the activated complexes.

The zwitterionic species $H_2O^+CH_2O^-$, which would be the expected intermediate in a stepwise mechanism for nucleophilic addition of a water molecule to formaldehyde, was predicted by ab initio self-consistent-field molecular-orbital (SCFMO) calculations at the STO-3G and 4-31G level to be unbound in the gas phase.[1,2] As the neutral reagents approach along the minimum-energy Bürgi–Dunitz trajectory,[3,4] their interaction is wholly repulsive for all separations less than ~2.4 Å.[2] Uncatalyzed formation of the product diol is enforced to proceed by a concerted mechanism involving a four-center activated complex **1** (Figure 1, curve U). A single ancillary water molecule may interact favorably with the reacting system by serving monofunctionally either as a hydrogen bond donor to the carbonyl oxygen (simulating general acid catalysis) or as a hydrogen bond acceptor from the nucleophilic water (simulating general base catalysis). The energy of all points along the uncatalyzed addition path is lowered by these interactions (Figure 1, curves A and B), which therefore provide for catalysis which may be described as *passive*: facilitation without significant alteration of the reaction coordinate.[1] However, the ancillary water molecule may also serve bifunctionally as both donor and acceptor of hydrogen bonds in a cyclic fashion **2**. Now the intervention of the extra molecule effects not only an energetic reduction but also profound change in the nature of the reaction coordinate for the addition (Figure 1, curve C). This catalysis may be described as *active*: facilitation by alteration of the reaction coordinate.[1]

Bifunctional participation of a single ancillary water molecule in a six-membered, cyclic activated complex for nucleophilic addition to carbonyl was first suggested by Syrkin[5] in connection with ester hydrolysis. (An earlier discussion of mechanisms for acid and base catalyzed ester hydrolyses by Laidler[6] had postulated cyclic activated complexes involving hydrogen bonding of a catalytic molecule to both nucleophile and nucleofuge but not to the carbonyl group.) Eigen[7] mentioned the possibility of cooperative mechanisms for proton transfer in aqueous solution involving bifunctional participation of *several* water molecules in

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