($C_{15}H_{14}{}^{81}BrN_2O_2S$, 42), 365 ($C_{15}H_{14}{}^{79}BrN_2O_2S$, 43.9), 340 ($C_{13}H_{11}{}^{81}BrN_2O_2S$, 43.4), 338 ($C_{13}H_{11}{}^{79}BrN_2O_2S$, 45.3), 182 ($C_8H_8NO_2S$, 32.7), 158 ($C_5H_3{}^{81}BrN$, 62), 156 ($C_5H_3{}^{79}BrN$, 62.7), 136 ($C_7H_6NS$, 100). Anal. Calcd for $C_{30}H_{28}Br_2N_4O_5S_2$: C, 48.13; H, 3.74; N, 7.49. Found: C, 47.97; H, 3.55; N, 7.49.

Reaction of 2,2-Bis(6′-bromo-2′-pyridyl)-1,3-dioxolane (7) with Ethanedithiol. The general procedure B was followed except for the substitution of ethanedithiol (235 mg, 2.5 mmol) and toluene as the solvent; heating was continued for 21 days. The cooled mixture was handled according to the standard procedure to afford two major components.

Fraction A was unchanged **7**: 215 mg (22%).

Fraction B yielded the symmetrical open chain **19** as a yellow oil: 16 mg (1%); ^1H NMR δ 4.13 (m, ketal CH_2, SCH_2), 7.17 (dd, 5-py H, $J = 7.9, 0.9$ Hz), 7.38 (dd, 5′-py H, $J = 7.9, 0.9$ Hz), 7.52 ndd, 4,4′-py H, $J = 7.9, 7.3$ Hz), 7.62 (dd, 3-py H, $J = 7.3, 0.9$ Hz), 7.69 (dd, 3′-py H, $J = 7.3, 0.9$ Hz); IR (neat) 1458, 1590 cm^{-1}; MS, *m/e* 230 ($C_8H_7{}^{81}BrNO_2$, 100), 228 (C_8,$H_7{}^{79}BrNO_2$, 96.8). Anal. Calcd for $C_{28}H_{24}Br_2N_4O_4S_2$: C, 47.73; H, 3.41; N, 7.95. Found: C, 47.47; H, 3.64; N, 8.25.

Reaction of 2,2-Bis(6′-bromo-2′-pyridyl)-1,3-dioxolane (7) with Bis(2-mercaptoethyl) Sulfide. Adherence to the general procedure except for the substitution of bis(2-mercaptoethyl) sulfide (385 mg, 2.5 mmol) and toluene as the solvent afforded only unchanged **7**.

Hydrolysis of Triethylene Glycol Ketal Macrocycle 8c. A General Procedure. A solution of **8c** (70 mg, 0.2 mmol), aqueous HCl (10 mL, 6 M), and MeOH (10 mL) was refluxed for 72 h. After concentration in vacuo, the acidic residue was neutralized carefully with aqueous Na_2CO_3 (10%) and extracted with $CHCl_3$ (4 × 50 mL). The combined organic extract was dried over $MgSO_4$ and concentrated to afford macrocyclic ketone **20b**, which was recrystallized from $CHCl_3$/EtOH to give colorless massive crystals. Pertinent data are shown in Table II.

Reduction of Diethylene Glycol Ketone Macrocycle (20a). A General Procedure. To an ice-cooled solution of **20a** (28 mg, 0.1 mmol) in MeOH (50 mL) was added solid $NaBH_4$ (380 mg, 10 mmol) at such a rate that the temperature did not rise above 10 °C. The mixture was stirred for 1 h at 20 °C, then refluxed for 12 h. After concentration in vacuo, an aqueous solution of Na_2CO_3 (20 mL, 10%) was added and the slurry was refluxed for 2 h. The cooled suspension was extracted with $CHCl_3$ (4 × 50 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and concentrated to give a yellow oil, which was chromatographed (ThLC) on silica; elution with 3% $MeOH/CHCl_3$ afforded carbinol macrocycle **23a** as a colorless oil. See Table III for critical data.

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Registry No. **6**, 42772-87-2; **7**, 42772-88-3; **8b**, 90867-41-7; **8c**, 90867-42-8; **8d**, 70091-61-1; **8e**, 70091-62-2; **8f**, 70091-63-3; **9a**, 90867-43-9; **9b**, 90867-44-0; **9c**, 90867-45-1; **9d**, 90867-46-2; **9e**, 90867-47-3; **9f**, 90867-48-4; **9g**, 90867-49-5; **10a**, 90886-00-3; **10b**, 90867-58-6; **11**, 90885-99-7; **12a**, 90867-59-7; **12b**, 90867-61-1; **13a**, 90867-60-0; **13b**, 90867-62-2; **13c**, 90867-65-5; **13d**, 90867-67-7; **14**, 90867-63-3; **15a**, 90867-64-4; **15b**, 90867-66-6; **16a**, 42772-88-3; **16b**, 90867-68-8; **17**, 90867-69-9; **18**, 90867-70-2; **19**, 90867-71-3; **20a**, 90885-98-6; **20b**, 90867-50-8; **20c**, 70100-65-1; **20d**, 70091-64-4; **20e**, 70091-65-5; **21a**, 90867-51-9; **21b**, 90867-52-0; **23a**, 90867-53-1; **23b**, 90867-54-2; **23c**, 90867-55-3; **23d**, 90867-56-4; **23e**, 90867-57-5; $BrCH_2CH_2OH$, 540-51-2; $(HSCH_2CH_2)_2O$, 2150-02-9; $HSCH_2CH_2SH$, 540-63-6; $(HSCH_2CH_2)_2S$, 3570-55-6; hexaethylene glycol, 2615-15-8; pentaethylene glycol, 4792-15-8; tetraethylene glycol, 112-60-7; triethylene glycol, 112-27-6; diethylene glycol, 111-46-6; ethylene glycol, 107-21-1.

Supplementary Material Available: The general MS fragmentation scheme for **8**; tables of fragmentation data for **8** and **9**; coordinates of nonhydrogen atoms for **8d**, **8b**, **20e**·H_2O, **20c**; bond distances and angles for **8d**, **8b**, **20e**·H_2O, **20c**; coordinates assigned to hydrogen atoms for **8d**, **8b**, **20e**·H_2O, **20c**; anisotropic thermal parameters for **8d**, **8b**, **20e**·H_2O, **20c** (17 pages). Ordering information is given on any current masthead page.

Structures and Stabilities of $C_2H_4N^+$ Isomers: An ab Initio Molecular Orbital Study

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Structures and energies of seventeen $C_2H_4N^+$ isomers were determined by semiempirical (MNDO) and various ab initio methods in order to get information concerning stabilities and reactivities of these ions. Among the C–N–C topologues the nitrilium ion **5** is predicted to be lowest in energy, ca. 9 kcal/mol lower than the 2-azaallenium ion **1** (at MP2/6-31G*//4-31G, the highest calculational level used throughout in this study). The most stable of the C–C–N isomers is the nitrilium ion **6**, which is the best of all $C_2H_4N^+$ isomers. Among the cyclic structures the iminium ion **12** is favorable, whereas the nitrenium ion **14** is the most energy rich of all isomers considered here. Some of the ions also possess low lying triplet states: the β-aminovinyl cation **11t**, the cyclic ion **14t**, and the carbene type ion **16t**. The interconversion of the $H_2C–N–CH_2^+$ topologues **14**, **2**, **3**, and **1** was studied using the C–N–C bond angle as the reaction coordinate. **14** is, if at all, only a very shallow minimum; structures **2** and **3** correspond to the transition states. The only experimentally accessible ion is predicted to be the 2-azaallenium ion **1** with an estimated automerization barrier of ca. 42 kcal/mol. Formally all the $C_2H_4N^+$ ions can be derived from protonation reactions of seven C_2H_3N molecules. The heats of protonation are evaluated to determine the thermodynamic basicity of the different molecules and the different molecular sites.

Azacarbenium ions, synthetically useful intermediates in a great variety of chemical reactions,[1,2] are also interesting because of the different ways in which the nitrogen atom can interact with the electron deficient carbenium center.[3] Simple iminium salts of type $R_2C{=}NR_2{}^+X^-$

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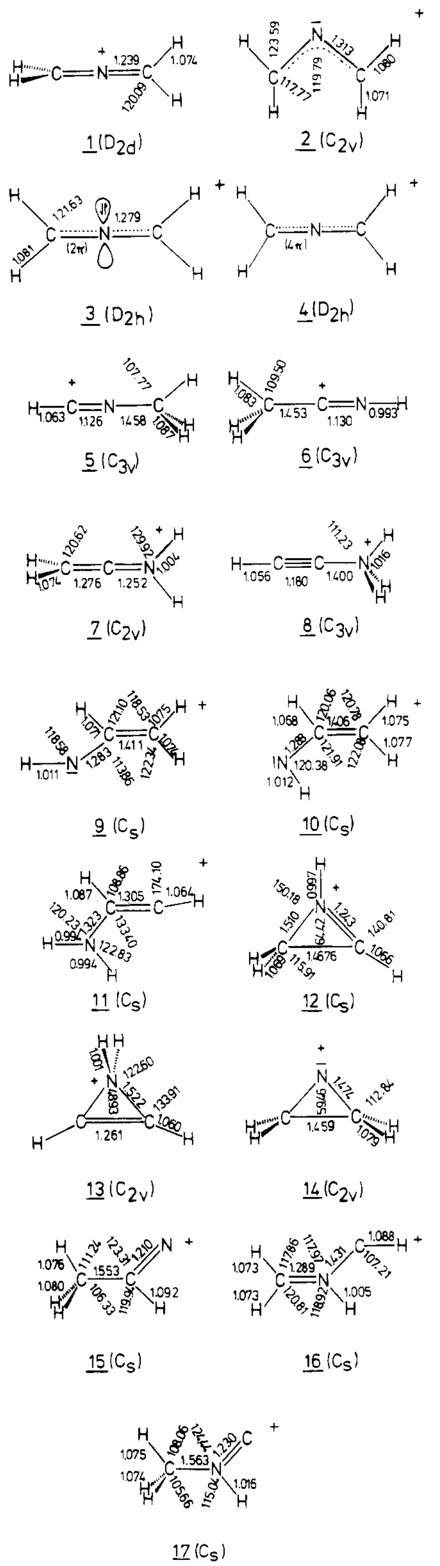

Figure 1. RHF/4-31G-optimized structures of singlet molecules (Å, deg).

(Mannich reagent,[2,4] Böhme salt[5]) are reactive aminoalkylating reagents, whose synthetic use can be widely expanded by appropriate substitution with electron-donor and electron-acceptor substituents.[2] The parent ion, $H_2C{=}NH_2^+$, is known experimentally.[6]

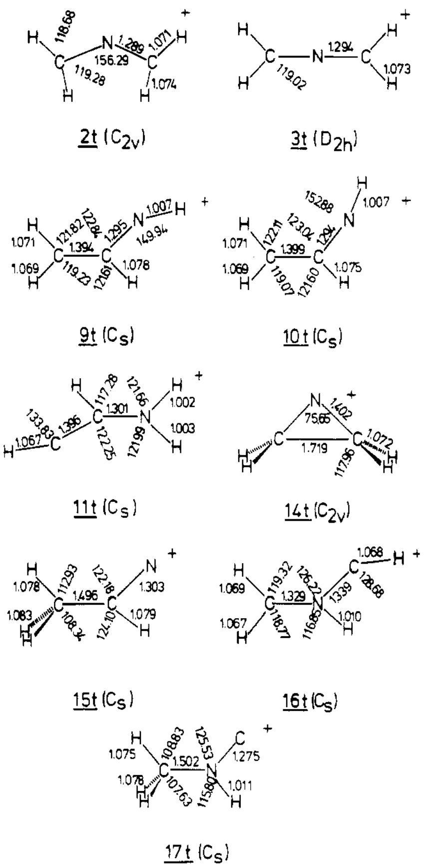

Figure 2. UHF/4-31G-optimized structures of triplet molecules (Å, deg).

In connection with experimental studies on 2-azaallenium ions,[7-9] which might be regarded as "double iminium salts", seventeen $C_2H_4N^+$ isomers were examined calculationally by using semiempirical and ab initio methods. The structures were determined, relative gas-phase stabilities were evaluated, and some predictions about chemical reactivity (acidity) and possible isomerizations of these ions have been made. The ions considered belong to three topological classes: we deal with C-N-C, C-C-N-, and three-membered heterocyclic isomers; chemically they include allene-, allyl-, nitrilium-, alkyne-, and heterocyclic systems. Due to the two double bonds carbene, nitrene, and nitrenium reactivity is expected for some of the isomers. Formally the $C_2H_4N^+$ molecules can be derived from protonation reactions of the corresponding C_2H_3N isomers. On the basis of thermodynamic data, predictions about the preferred protonation site are presented.

Methods and Results

Ab initio molecular orbital calculations were carried out at the restricted and unrestricted Hartree-Fock level by using the Gaussian 76 series of programs.[10] The structures of all molecules were optimized (within the indicated point group) by using analytical force evaluation routines[11] and

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Table I. Calculated Heats of Formation (MNDO, kcal/mol), Total Energies (ab Initio, au), and Relative Energies (kcal/mol)

	species	symm	MNDO	rel	4-31G// 4-31G	rel	6-31G*// 4-31G	rel	MP2/ 6-31G*// 4-31G	rel
1	2-azaallenium ion	D_{2d}	212.29	0.00	−132.01960	0.00	−132.21428	0.00	−132.60738	0.00
2	2-azaallyl cation	C_{2v}	235.83	23.54	−131.95396	41.19	−132.16593	30.34	−132.54031	42.09
2t	2-azaallyl cation trip	C_{2v}	262.58	50.29	−131.95370	41.35	−132.14706	42.18	−132.49627	69.72
3	2-azaallyl cation (2π)	D_{2h}	246.49	34.20	−131.91440	66.01	−132.11173	64.35	−132.48586	76.25
3t	2-azaallyl cation trip	D_{2h}	262.83	50.54	−131.95232	42.21	−132.14513	43.39	−132.49504	70.50
4	2-azaallyl cation (4π)	D_{2h}								
5	*N*-methylnitrilium ion	C_{3v}	212.56	0.27	−132.02475	−3.23	−132.22164	−4.62	−132.62242	−9.44
6	N-protonated acetonitrile	C_{3v}	207.39	−4.90	−132.04452	−15.64	−132.23640	−13.88	−132.63618	−18.07
7	keteniminium ion	C_{2v}	216.99	4.70	−132.02699	−4.64	−132.21096	2.08	−132.60361	2.37
8	ethinylammonium ion	C_{3v}	232.02	19.73	−131.98339	22.72	−132.16639	30.05	−132.57141	22.57
9	1-azaallyl cation exo	C_s	250.64	38.35	−131.94866	44.51	−132.14671	42.40	−132.52648	50.76
9t	1-azaallyl cation exo trip	C_s	264.76	52.47	−131.97793	26.15	−132.16451	31.23	−132.50273	65.67
10	1-azaallyl cation endo	C_s	257.39	45.10	−131.93383	53.82	−132.13066	52.47	−132.51175	60.01
10t	1-azaallyl cation endo trip	C_s	264.77	52.48	−131.97712	26.66	−132.16360	31.80	−132.50145	66.47
11	*β-amino vinyl cation*	C_s	262.53	50.24	−131.94641	45.93	−132.13048	52.58	−132.50632	63.41
11t	β-amino vinyl cation trip	C_s	251.57	39.28	−131.99442	15.80	−132.18002	21.50	−132.52762	50.05
12	1-azirinium ion	C_s	244.80	32.51	−131.95591	39.96	−132.16757	29.31	−132.56930	23.89
13	2-azirinium ion	C_{2v}	250.52	38.23	−131.95133	42.85	−132.15544	36.92	−132.56135	28.88
14	1-aziridinyl cation	C_{2v}	306.83[a]	94.54	−131.84759	107.93	−132.06610	92.98	−132.44032	104.83
14t	1-aziridinyl cation trip	C_{2v}	295.38	83.09	−131.88797	82.60	−132.10702	67.31	−132.46795	87.49
15	C-protonated acetonitrile	C_s	279.52	67.32	−131.92475	59.52	−132.12371	56.83	−132.49831	68.44
15t	C-protonated acetonitrile trip	C_s	306.56	94.37	−131.88634	83.62	−132.07426	87.86	−132.40171	129.06
16	*N*-iminium carben	C_s	279.11	66.82	−131.92258	60.88	−132.11945	59.50	−132.48415	77.33
16t	*N*-iminium carben trip	C_s	263.63	51.34	−131.96947	31.46	−132.15851	34.99	−132.49754	68.92
17	N-protonated methyl isocyanide	C_s	271.63	59.34	−131.95065	43.27	−132.14282	44.84	−132.51848	55.78
17t	N-protonated $H_3C–NC$ trip	C_s	338.30	126.01	−131.90714	70.56	−132.09383	75.58	−132.42683	113.29

[a] C–N–C bond angle restricted to 60°.

Table II. Calculated Heats of Formations (MNDO, kcal/mol), Total Energies (4-31G//4-31G, au), and Relative Energies (kcal/mol) of C_2H_3N Molecules and Their Protonation Reactions[a] (ΔH_r, kcal/mol)

	species	symm	MNDO	rel	4-31G//4-31G	rel	product ion	ΔH_r MNDO	ΔH_r 4-31G//4-31G
18	nitrile ylide	C_s	83.2	64.3	−131.61607	70.42	1	$\underline{-237.9}$	−253.21
							5	−237.6	$\underline{-256.44}$
							16	−171.1	−192.33
19	methyl isonitrile	C_{3v}	60.0	41.2	−131.69421	21.39	5	$\underline{-214.4}$	$\underline{-207.41}$
							17	−155.4	−160.91
20	acetonitrile	C_{3v}	18.9	0.0	−131.7283[b]	0.00	6	$\underline{-178.5}$	$\underline{-198.42}$
							15	−106.4	−123.27
21	ketenimine	C_s	47.0	28.2	−131.6731[b]	34.64	6	$\underline{-206.6}$	$\underline{-233.06}$
							7	−197.0	−222.06
							9	−163.4	−172.91
							10	−156.6	−163.61
22	aminoacetylene	C_{2v}	55.9	37.0	−131.6616[b]	41.85	7	$\underline{-205.9}$	$\underline{-229.28}$
							8	−190.9	−201.92
							11	−160.4	−178.72
23	1-azirine	C_s	68.5	49.7	−131.6119[b]	73.04	12	$\underline{-190.7}$	$\underline{-215.86}$
							14	−128.7	−147.89
24	2-azirine	C_s	85.5	66.7	−131.55981[c]	105.72	12	$\underline{-207.7}$	$\underline{-248.55}$
							13	−202.0	−245.67

[a] MNDO$\Delta H_f(H^+)$ = 367.0 kcal/mol. [b] Ref 64. [c] Ref 51.

the split-valence basis set 4-31G.[12] The optimized structures of the singlet molecules are represented in Figure 1. Triplet states[18] were included when resonance structures of carbene, nitrene, or nitrenium types suggested some extra stabilization leading to comparable singlet and triplet total energies (Figure 2). MNDO structures[13] were taken as starting geometries for the ab initio optimizations.

Improved energies were obtained from higher level single-point calculations employing the polarization 6-31G* basis set.[14] Valence electron correlation was incorporated via second-order (MP2) Møller-Plesset perturbation theory.[15] The notation MP2/6-31G*//4-31G designates a MP2 (Møller-Plesset) electron correlation correction applied to a 6-31G* SCF calculation using the optimized 4-31G geometry.

Total and relative energies of the cations at all calculational levels (including MNDO) are given in Table I. Triplets are indicated by the letter "t" (e.g., 16t). In Table II heats of formation (MNDO) and total and relative energies (4-31G//4-31G) of C_2H_3N molecules are summarized, together with the heats of reactions of some of the possible protonation reactions. Calculational simulation of the electrocyclic ring-opening process of the aziridinyl cation **14** was carried out by using the 4-31G basis set and by optimizing the complete structures except for the C–N–C bond angle which was chosen as the reaction coordinate (Figure 3).

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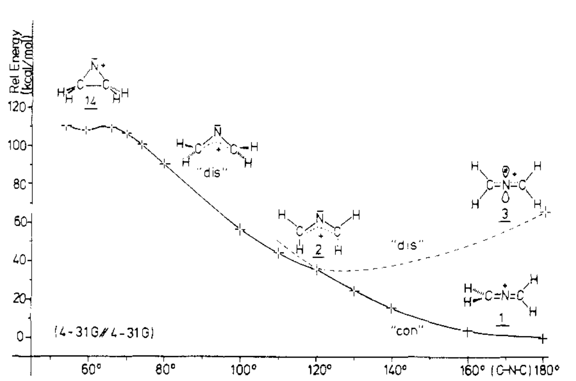

Figure 3. Electrocyclic ring opening of 1-aziridinium ion **14**. RHF/4-31G relative energies (kcal/mol) in dependence on the C–N–C bond angle (deg).

Charge distributions of the cations are based on Mulliken population analysis[16] of the 4-31G wave functions. Although basis set dependence and other deficiencies of this method are well-known,[17] comparisons between isomeric cations should give useful information related to chemical reactivity. In all cases total charges (not π-charges) are given. In the discussion the highest computational level is always used.

Discussion

2-Azaallenium Ion 1 (D_{2d}). Among the $C_2H_4N^+$ isomers with H_2C-N-CH_2 topologies the cation **1** (D_{2d}) is lowest in energy and is taken as the reference (E_{rel} = 0.00 kcal/mol) to which the energies of the other ions are related. The C=N bond length in **1** (1.239 Å) is found to be substantially shortened compared to the corresponding bond length of the iminium ion $H_2C{=}NH_2^+$ ($r_{C=N}$ 1.268 Å),[19] due to the sp hybridization of the central nitrogen atom. Analogous trends are found in the C=C bond lengths in allene and in ethene (1.294 vs. 1.320 Å).[19] In spite of the formal positive charge in **1** the central nitrogen atom is indicated to be negative (–0.560) due to its electronegativity.[20] Consequently, the methylene groups carry very high positive charges (+0.760 for each CH_2) and high electrophilic reactivity is expected at these termini. The charges in **1** are much more unevenly distributed than in the iminium ion $H_2C{=}NH_2^+$ (CH_2 +0.775, NH_2 +0.225). Since the iminium ion is known to be a powerful electrophile (Mannich[2,4] Böhme reagent[5]), which is often used in synthetic organic chemistry, even higher electrophilic reactivity is expected for ion **1**. In allene, the charge on the central carbon atom is essentially zero. The unsubstituted ion **1** is not known experimentally. Substituted derivatives, however, which are more stable thermodynamically and kinetically, have been recently synthesized.[7-9,22-24] The evaluation of the synthetic potential of these ions is under investigation.[21] Ions of type **1** are possible intermediates in a number of reaction mechanisms[25,26] and have been observed mass spectroscopically.[27,28] An X-ray structure analysis of a tetraaryl-substituted derivative confirms the orthogonal arrangement of the two methylene units, although the central C–N–C angle is reduced to 163° in this heavily substituted ion.[29]

The Bent 2-Azaallyl Cation 2 (C_{2v}). This second H_2C–N–CH_2 topomer, **2** may be considered to be an allyl cation, whose central CH unit has been replaced by nitrogen. The energy of this ion (constrained to be planar during optimization) is 42.1 kcal/mol higher than that of **1**. Like the allyl cation, ion **2** has two π-electrons and in addition a sp^2 lone pair of nitrogen in the molecular plane. With bond order 1.5 the C–N bonds are longer than in **1** (1.313 Å). The charge distribution is similar to **1**: CH_2 +0.750, N –0.500. The parent ion **2** (or simple substituted derivatives) does not correspond to a minimum but rather to a transition state on the hyperface (see below). The superior stability of **1** compared to **2** can be derived from a molecular orbital correlation[29] where the b_2 type σ orbitals came out to be responsible for better bonding in the linear form.

However, strong electron-donor groups (especially amino groups) lower the relative energy of these 2-azaallyl cations so much that they become more favorable than the corresponding isomers of the allene type **1**.[29] Indeed, molecules like the ionic 1,3-bis(dimethylamino)-2-azaallyl chloride[30] and other so called azapolymethine dyestuff molecules[31-33] are well-known experimentally; the planar C_{2v} structure is shown by X-ray measurements.[34] Ion **2** does not have a low lying triplet state. At the highest computational level employed a C_{2v} triplet molecule, **2t**, was found to have a relative energy of 69.7 kcal/mol. Therefore, thermal reactions of ion **1** or **2** are not likely to proceed via triplet states. Since the relative energy of **2t** is high compared to **2**, also no low lying open-shell singlet with a relative energy close to the one of **2** has to be expected; MNDO finds an open-shell singlet minimum with a relative energy of 51.2 kcal/mol.

The Linear 2-Azaallyl Cations 3 and 4 (D_{2h}). Further restriction of symmetry on the point group D_{2h} gives the linear H_2C–N–CH_2 topomers **3** and **4**. Two lumomeric[35] forms are possible: in **3**, there is a p lone pair on nitrogen. The relative energy of **3** is 76.3 kcal/mol; this ion corresponds to a saddle point on the hyperface rather than to a minimum (see below). The second lumomeric form, **4**, has four π-electrons in the ψ_1 and ψ_2 allyl orbitals; the p orbital on nitrogen remains empty. The energy of this form, which could not be calculated explicitly, is expected to be considerably higher than that of **3**. The calculated energy difference between ion **2** and **3** (34.2 kcal/mol) indicates how much a nitrogen atom prefers a sp^2 lone pair over a lone pair in a pure p orbital. Singlet ion **3** is so rich in energy, that a triplet state **3t** becomes

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competitive (E_{rel} = 70.5 kcal/mol). Since the bent triplet **2t** is only 0.8 kcal/mol lower in energy than **3t** this part of the triplet hyperface is predicted to be very flat leading to exceptional structural flexibility of these excited ions.

N-Methylated Cyanic Acid 5 (C_{3v}). Together with ion **6**, system **5** belongs to the class of nitrilium ions. These are well-known from experimental[1,36] and from theoretical[3b] studies. Structural details have been determined by X-ray crystallography.[37]

5 is 9.4 kcal/mol *lower* in energy than reference ion **1**; the calculated C–N bond length (1.126 Å) is typical for a C≡N triple bond and agrees well with the X-ray data (1.132 Å) of a substituted derivative.[37] The nitrogen atom also bears considerable negative charge (–0.482) in this cation, the methyl group (+0.643) and the methine function (+0.839) distributing the positive charge.

In spite of the greater stability of **5** compared to **1**, a spontanous isomerization of the latter in the gas phase is not to be expected. According to the Woodward–Hoffmann rules[38] suprafacial 1,3-shifts are forbidden and a high activation barrier for the intramolecular process is predicted.[28,39] Stepwise isomerization via nitrile ylides by deprotonation–protonation of derivatives of **1** does not lead to nitrilium ions in condensed phase because of side reactions of the intervening nitrile ylide.[21]

N-Protonated Acetonitrile 6 (C_{3v}). The nitrilium ion **6**, the first of the C–C–N topomers **6–11**, possesses the lowest total energy of all seventeen C$_2$H$_4$N$^+$ isomers of this study: E_{rel} = –18.1 kcal/mol, relative to **1**. This ion is well-known experimentally from studies of acetonitrile in strongly acidic solutions.[40] Protonation at the nitrile carbon atom is much less favorable (ion **15**, see below). The superior stability of ion **6** compared to **5** is mainly due to better hyperconjugative interaction of the methyl group with the electron deficient (+0.719) nitrilium carbon atom. The methyl group has a total charge of +0.411; the nitrogen atom is very negative: –0.692. (For the basicity of acetonitrile, see below.)

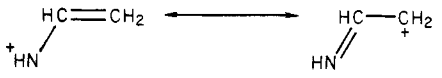
Keteniminium Ion 7 (C_{2v}). Substituted keteniminium ions are valuable synthetic reagents, whose cycloaddition reactions provide access to many interesting heterocyclic systems.[41] In analogy to **1**, ion **7**, which could also be named the 1-azaallenium ion, shows the typical orthogonal arrangement of two π-bonds of allene-type molecules. The relative energy of **7** (+2.4 kcal/mol) is only a little higher than that for **1**. The structural features of an iminium ion and of an allene are combined in **7**, as can be seen from its bond lengths and angles (Figure 1).

The charge distribution in **7** is fundamentally different from that calculated for **1**. Therefore significant differences in chemical behavior are to be expected. The NH$_2$ group bears little positive charge (+0.065); the central carbon may be the most electrophilic site (+0.479), but the terminal methylene function is indicated to be only slightly less electron deficient (+0.455). The ions **9**, **10**, and **11** show a similar charge distribution. (See below.)

The structure of a substituted keteniminium salt is known experimentally from an X-ray study;[42] the geometrical data, especially the linear C_{2v} arrangement, are in close agreement with the calculated parameters. Keteniminium accessible from α-halogen enamines[41] and are employed synthetically as isolated salts or can be generated and trapped in situ.[41] The parent neutral system of **7**, ketenimine,[63] was the subject of theoretical studies concerning its structure, reactivity, and hydrolysis.[43]

Ethynylammonium Ion 8 (C_{3v}). Isomer **8** contains a C–C triple bond fragment, which is thermodynamically unfavorable, especially in comparisons to C–N triple and double bond systems. Therefore, **8** is less stable than ion **7** (E_{rel} = 22.6 kcal/mol). Substituted derivatives of **8** are known experimentally,[44] but the parent system as well as all species having amine protons are not stable in condensed phases. Rearrangements via keteniminium ions (like **7**) lead to the most stable C–C–N isomers, the nitrilium salts (like **6**). Analogous isomerizations are known: ethynylamines rearrange via keteneimines to yield nitriles[44a] and hydroxy acetylenes give ketenes. No unexpected structural features are calculated for **8**. The charge distribution, however, differs from the other C$_2$H$_4$N$^+$ isomers: significant positive charge is located at the ammonio group (+0.522) and at the HC terminus (+0.468), whereas the central carbon atom is almost free of charge (+0.010). In this respect, **8** resembles the allene type ion **1** or enammonium ions.[21]

***exo*- and *endo*-1-Azaallyl Cations 9 and 10 (C_s).** Like the 2-azaallyl cation **2** the 1-azaallyl cations **9** and **10** are energy rich C$_2$H$_4$N$^+$ isomers. The exo form **9** is more stable (E_{rel} = 50.8 kcal/mol) than the *endo*-**10** (60.0 kcal/mol). The instability of these ions is also indicated by the unfavorable resonance contributors, nitrenium ion **9/I** and the α-imino cation form **9/II**. The isoelectronic carbonylmethyl cation H$_2$$^+$CCH=O is a destabilized methyl cation for similar reasons.[45]



9/I **9/II**

Both **9** and **10** are electron deficient at the CH$_2$ terminus (**9** +0.670), the central CH unit (+0.254) and the NH function (+0.076) are less positive. This charge distribution corresponds more to the α-imino methyl cation form **9/II**.

To our knowledge isolated 1-azaallyl cations have not been observed directly; nevertheless α-halogeno imines are valuable precursors for the in situ generation of derivatives of **9** and **10**.[46,47] Nitrenium structure **9/I** implies low lying triplet states. At the highest calculational level employed triplets were found whose energies are comparable to energies of the singlets mentioned before (**9t** E_{rel} = 65.7, **10t** E_{rel} = 66.5 kcal/mol). This suggests interesting experimental studies on possible ground-state diradicaloid reactivity.

***β*-Amino Vinyl Cation 11 (C_s).** Ion **11** is one of the less stable C$_2$H$_4$N$^+$ isomers (E_{rel} = 63.4 kcal/mol); nevertheless its derivatives can easily be generated in situ from β-

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halogen enamines.[48] They are valuable intermediates in organic synthesis.[48] Theoretical calculations were included in a study of the effect of β-substituents on vinyl cations.[49] C–C (1.305 Å) and C–N (1.323 Å) bond lengths are comparable, indicating some allylic conjugation as was found in the 1-azaallyl cations **9** and **10**. In the optimized minimum structure the terminal C–H is slightly bent away from the amino substituent, giving a transoid conformation. The positive charge is concentrated in the vinyl part of the ion (=CH 0.547, —CH= 0.416). The amino group as a whole is almost uncharged (+0.037), but the nitrogen atom is very negative (−0.843) due to its electronegativity, the amino hydrogen atoms compensating this negative charge. A search for a second minimum with the amino group perpendicular to the vinyl plane resulted in the formation of the three-membered ring system **13**, which is much lower in energy (see below).

The high relative energy and the carbene resonance structure of **11** prompted us to look for low lying triplet states. Indeed, a minimum was found whose total energy ($E_{\rm rel}$ = 50.1 kcal/mol) surprisingly was much lower than that of the corresponding singlet molecule. This form is best regarded as a triplet *C*-iminiumcarbene (long C–C bond (1.396 Å), short C–N bond (1.301 Å)).

1-Azirinium Ion 12 (C_s). Isomers **12**–**14** all have three-membered rings. **12** and **14** are N- and C-protonated derivatives of 1-azirine, the more stable of the two azirine isomers.[50,51] Similarly **13** can be considered to be N-protonated 2-azirine. Isomer **12** is implicated to be the reactive intermediate in acidic and superacidic solutions of 1-azirine.[50] Its relative energy (+23.9 kcal/mol) reflects the ring strain of this system, otherwise the structural features are similar to those of an open-chain iminium ion. The C–N–C bond angle is widened to 64.4° because of the adjacent C=N double bond. Both carbons centers are very electrophilic: CH_2 carries +0.500 and CH carries 0.670 charge units; the iminium center is negatively charged (−0.170).

2-Azirinium Ion 13 (C_{2v}). Protonation of 2-azirine removes the Hückel antiaromatic character; this is reflected in the very high calculated proton affinity of 2-azirine for its N-protonation giving ion **13**: 245.7 kcal/mol.[51] Aziridine has an experimental proton affinity of 215.7 kcal/mol.[52] The relative energy of **13** (28.9 kcal/mol) is similar to **12**; ring strain again results in the remarkable 48.9° C–N–C bond angle, which is reduced because of the opposite C=C double bond (1.261 Å). The C–N single bonds are somewhat lengthened to 1.522 Å compared with unstrained systems. The CH groups are positively charged (+0.439), and the H_2N group carries a charge of +0.122; **13** is best regarded as a strained enammonium ion.

1-Aziridinyl Cation 14 (C_{2v}). The cyclic ion **14** is the most energy rich of all isomers considered here ($E_{\rm rel}$ = 104.8 kcal/mol). Besides the ring strain (ca. 30 kcal/mol), the six-electron character on nitrogen causes the enormous high energy content of this nitrenium ion.[53,54]

Despite the high relative energy and its expected instability, ion **14** may be an interesting local minimum on the H_2C–N–CH_2^+ hyperface (see below): electrocyclic ring opening gives the topomeric ions **3**, **2**, and **1**. *N*-halogenaziridine precursors may lead to the in situ generation of such ions; subsequent reactions give products which are in agreement with such intervening ions.[53]

The C–N bond length (1.474 Å) and the C–N–C bond angle (59.5°) in **14** are as expected. Surprisingly the charge distribution of **14** resembles that of **13**: the methylene groups carry a total charge of +0.43, and that on the nitrenium nitrogen atom is +0.139.

The nitrenium character of this ion suggests favorable triplet states: a minimum ($E_{\rm rel}$ = 87.5 kcal/mol) was located on the triplet hyperface, lying ca. 17 kcal/mol lower than the singlet molecule. Although direct comparison between states of different multiplicities are always difficult, such a big difference must be taken as a strong indication for a favorable diradicaloid species. Surprising are the structural properties of this triplet: the C–N–C angle is widened to 75.7°, and the C–C bond (1.719 Å) obviously has only very little bonding character. The C–N bonds are shorter (1.402 Å) than in the singlet molecule.

C-Protonated Acetonitrile 15 (C_s). The ions **15**–**17** are all energy rich, more or less exotic $C_2H_4N^+$ isomers which have not been observed experimentally. Ion **15** is the less favored product of protonation of acetonitrile, taking place at the carbon atom, with a relative energy of 68.4 kcal/mol. N-Protonation of acetonitrile gives the much more stable nitrilium ion **6** (vide supra). In **15**, the C–C bond is unusually long (1.553 Å) whereas the C–N bond (1.210 Å) may be regarded as a strong double bond. Therefore, **16** possesses the structural features of a nitrenium ion[53,54] ("C-methylated cyanic acid"). The positive charge is concentrated in the carbon part of the molecule: CH_3 0.464, CH 0.408, N 0.168. Analogous to vinylidine,[55] this nitrenium ion **15** does *not* have a low lying triplet state (**15t** $E_{\rm rel}$ = 129.1 kcal/mol). As in other carbene and nitrenium molecules (see **17**) the double bond to the six-electron atom (C or N) disfavors triplet states because of the big separation between HOMO and LUMO (sp and p orbitals, respectively).

***N*-Iminio Carbene 16 (C_s).** Ion **11** (especially the triplet state **11t**) was regarded as a C-connected iminium carbene. Similarly, ion **16** is best understood as *N*-iminium carbene. Its relative energy is high ($E_{\rm rel}$ = 77.3 kcal/mol). Routes to its experimental realization have, to our knowledge, not been developed. The structural properties of the iminium part of **16** (C–N 1.289 Å) are close to those of the iminium ion $H_2C{=}NH_2^+$ itself; the carbene part is separated by a 1.431-Å C–N single bond. Very unfavorable charge distribution is found from the Mulliken analysis: +0.888 for CH_3, −0.351 for NH, and +0.463 for CH.

As expected for such a carbene type molecule there is also a low lying triplet minimum on the hyperface ($E_{\rm rel}$ = 68.9 kcal/mol compared to **1**). In this ion **16t**, bond lengths and charges are somewhat better balanced than in the corresponding singlet molecule.

N-Protonated Methyl Isonitrile 17 (C_s). Like ion **15**, which is the less favorable protonation product of acetonitrile, ion **17** is the more energy rich protonation product of methyl isocyanide (compare **5** for the C-protonation product). In comparison to other $C_2H_4N^+$ isomers its relative energy (55.8 kcal/mol) gives little hope for experimental realization. The structure may best be regarded as N-methylated isocyanic acid HN=C, since the methyl group is unusually weakly bonded (C–N 1.563 Å). The C=N bond, however, shows much double bond character (1.230 Å). Again, the charges are very unevenly distributed: CH_3 +0.614, NH −0.325, C +0.710. As in **15**,

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no low lying triplet minimum was found; here again, the six-electron atom (carbon) is doubly bonded to a sp^2 center so that HOMO (sp orbital) and LUMO (p orbital) of the singlet 17 are fairly separated and so unpairing of the electrons is unfavorable (E_{rel} = 113.3 kcal/mol for 17t).

The Electrocyclic Ring Opening of the 1-Aziridinyl Cation 14. Four of the $C_2H_4N^+$ isomers (1, 2, 3, and 14) show as a common feature the $H_2C-N-CH_2^+$ topology. The mutual interconversion of these ions can be studied by using the C–N–C bond angle as the reaction coordinate. Figure 3 displays the dependence of the relative energy (4-31G//4-31G) on the C–N–C bond angle (in the range from 56° to 180°). Earlier theoretical studies were carried out by Weiss,[56] Maier,[57] and Balli[58] (MINDO-3). Small C–N–C-angles are associated with very high relative energies (ca. 56–80°). At the 4-31G//4-31G level the aziridinyl cation 14 is only a shallow local minimum (near 59°). The energy barrier toward ring opening is calculated to be only 1.7 kcal/mol. Since minimal-(STO-3G gives a barrier of 11.5 kcal/mol) and medium-size basis sets are known to prefer cyclic structures,[59] its is quite likely, that at higher computational levels this barrier vanishes altogether. Interestingly, MNDO does not find a minimum for 14. So, ion 14 and its simple derivatives are unlikely to be capable of experimental isolation or spectroscopic study. However, precursor molecules like *N*-halogenoaziridines may give access to other $C_2H_4N^+$ isomers via 14, especially to ion 1.[25,53]

From C–N–C angles 70–120° the three-membered ring opens smoothly in a disrotatory mode.[38] At about C–N–C = 120°, the planar 2-azaallyl cation 2 is reached, but this form is not related to a minimum on the hyperface. However, 2 is characterized as a saddle point (minimum structure, if the geometry is restricted to C_{2v} or C_s). Further disrotatory angle widening leads uphill to the planar, linear ion 3 (a potential minimum only if the symmetry is restricted to D_{2h}). On the other hand, conrotatory methylene rotation lowers the energy further and at 180° the lowest point (global minimum) of the energy surface is reached, the 2-azaallenium ion 1.

To summarize, Figure 3 shows clearly that for thermodynamic reasons 1 is the only accessible $H_2C-N-CH_2^+$ isomer; structures 2, 3, and 14 (also 4) represent high energy transition states. A possible pathway for the racemization of chiral derivatives (C_2 symmetry[7]) of 1 can be predicted from Figure 3: direct rotation of one of the methylene units via 3, by keeping the linear C–N–C arrangement, is energetically disfavored over conrotatory rotation of both methylene groups accompanied by C–N–C bending. At C–N–C ~120°, the transition state of the racemization process (ion 2) is reached, and the chirality is lost. So we predict an isomerization barrier of about 42 kcal/mol (MP2/6-31G*//4-31G) for the unsubstituted system 1. Electron-donor substituents are predicted to lower this barrier considerably or even to favor planar structures like 2,[29] since the LUMO of the allyl form 2 (π^* orbital, $1a_2$) is a much better electron acceptor than the LUMO of the allene type molecule 1 (π^* orbital, 3e). For allene C_3H_4, a racemization process via an open-shell singlet transition state was proposed: 50.1 kcal/mol was the final value for the activation barrier via the bent transition state.[60] In the $C_2H_4N^+$ series however, low lying open-shell singlet states are not expected, since the corresponding triplet states (2t, 3t) are high in energy.

Interestingly, replacement of the central carbon atom in allene by a more electronegative atom (here nitrogen) *lowers* the rotational barrier. For the corresponding oxygen dication $H_2C-O-CH_2^{++}$, which is isoelectronic with allene and 1, a barrier of only 8.2 kcal/mol was calculated (MP2/6-31G*//3-21G).[21,61]

$C_2H_4N^+$ Molecules from Protonation Reactions of C_2H_3N Isomers. The seventeen isomeric cations 1–17 can formally be regarded as the result of protonation reactions of seven C_2H_3N molecules:[21,43] the nitrile ylide 18, methyl isonitrile 19, acetonitrile 20, ketenimine 21, aminoacetylene 22, and 1- and 2-azirine 23 and 24, respectively. All the possible protonation reactions are summarized in Table II together with MNDO and 4-31G//4-31G heats of reactions (kcal/mol). From these data the thermodynamically prefered site of protonation of the C_2H_3N isomers 18–24 can be predicted. Only singlet molecules have been considered.

The nitrile ylide 18,[62] which has not been observed experimentally, is predicted to be basic mainly at the carbon termini. Formation of product ion 5 is slightly favored over ion 1. Protonation on nitrogen is much less likely because of the very energy rich product, ion 16. Methyl isonitrile 19 should be a weak carbon base giving ion 5; ion 17, the N-protonation product, should not be formed under equilibrium conditions. Similary, acetonitrile 20 is also protonated at the terminus (nitrogen atom) giving the stable nitrilium ion 6; again, protonation at the central carbon atom to 15 is unfavorable. Ketenimine 21[63,64] gives access to the ions 6 and 7.[43] The formation of nitrilium ion 6 is favored by 11 kcal/mol over the formation of the keteniminium ion 7; again, protonation of the central C atom may be excluded. Interestingly, aminoacetylene 22 is predicted to be a stronger base at the carbon terminus than at the amino group, so leading to ion 7 and not to ion 8 (compare vinylamine[65]). Because of the thermodynamic instability of ion 11, its formation is unlikely in a protonation reaction of 22.

1-Azirine 23[50] is a nitrogen base of moderate strength; the formation of the CH protonation product, the nitrenium ion 14, can be excluded because of the very unfavorable total energy of this ion, which may not even be a minimum (see above). The antiaromatic, hitherto unknown 2-azirine 24[51] has two basic centers of almost equal basicity. Both protonation reactions (to 12 and 13) remove the antiaromatic character of 24. The calculated heats of reactions are very high (24 is a strong base), although both product ions still suffer from considerable ring strain.

Conclusions

The group of $C_2H_4N^+$ isomers consists of numerous ions, which are of great synthetic, structural, spectroscopic, and theoretical interest. The calculations, presented in this paper, should provide the theoretical background for future experimental work, not only on the parent ions, but also on more substituted derivatives.

Among the seventeen $C_2H_4N^+$ isomers the nitrilium ions 5 and 6 are lowest in energy. This reflects the favorable electronic interactions of a C–N triple bond and the op-

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timum charge distribution in these ions, compared to a C–C triple bond. The ability of the electronegative nitrogen atom to accomodate a favorable lone pair of electrons in sp^2, sp^3, and p orbitals adds to the structural versatility of these ions compared to the isoelectronic series of C_3H_4 compounds. The allenic structures **1** and **7** are ca. 20 kcal/mol higher in energy being still interesting targets for experimental realization. Higher total energies were found for the ethynylammonium ion **8** and for the cyclic ions **12** and **13**. The other ions considered in this study have high relative energies; thus they are expected to be highly reactive intermediates (**9**, **10**, **11**, **15**, **16**, and **17**), which should allow, via in situ generation, valuable synthetic transformations.

A more detailed study of the $H_2C–N–CH_2^+$ hyperface has shown, that in this series of ions only ion **1** corresponds to a minimum, whereas **2**, **3**, **4**, and **14** are indicated to be high energy transition states. The racemization process of chiral derivatives of **1** is predicted to proceed via ion **2**; the barrier for **1** was calculated to be ca. 40 kcal/mol. Some of the energy rich isomers have competitive triplet states: **9**, **10**, **11**, **14**, and **16**, which may contribute to ground-state reactivity. The semiempirical MNDO method performs remarkably well: trends and relative energies are in good agreement with the ab initio data (even for singlet–triplet comparisons).

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Solid- and Liquid-Phase Photodimerizations of 5*H*-Indolo[1,7-*ab*][1]benzazepine

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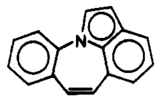
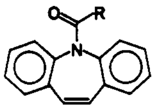
Unlike other dibenzazepines which give only anti photodimers, 5*H*-indolo[1,7-*ab*][1]benzazepine (1) gives a 3:1 ratio of "mirror plane" syn dimer 4 to "twofold axis" syn dimer 5 in the solid state and a 1:3 ratio of 4 to 5 in solution. Eximers are probably responsible for these syn dimers being formed. 4 and 5 crystallize isomorphously, the latter with spontaneous resolution. Unlike the anti dimers, which have planar cyclobutane rings in the crystal, the syn dimers have strongly twisted cyclobutane rings.

The 2 + 2 photodimerization of alkenes to cyclobutanes is a long-known reaction of current importance in applications such as solar to chemical energy conversions and the photocrosslinking of polymers.[1] We have found **1**, prepared in a study of imipramine and promazine analogues,[2] to be so prone to photochemical dimerization that it is difficult to keep in the monomeric form. Even indirect sunlight rapidly converts **1** (mp 113–114 °C) into a 3:1 mixture of two dimers, and solutions of **1** into the same two dimers but in the reverse ratio. Other dibenz[*b*,*f*]azepines **2** have recently been shown to give exclusively anti dimers **3**.[3] We wish to present evidence that **1** gives only syn dimers **4** and **5**, with **4** favored in the solid-phase dimerization and **5** predominating in solution, and to give possible reasons for the differing stereo- and regiochemistry in these dimerizations.



1



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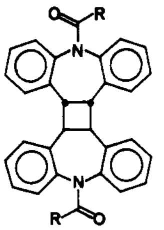

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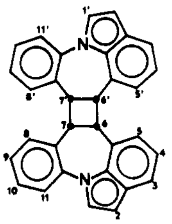

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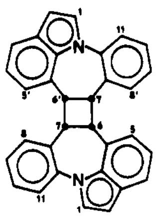

5

The two dimers obtained from **1** were separated by fractional crystallization. While their characteristic ^1H NMR spectral patterns served well as fingerprints, we could not safely use them to make stereochemical assignments, and thus carried out an X-ray study on each dimer.

Experimental Section

A 450-W Hanovia medium-pressure mercury lamp (Pyrex filter) was used for the photolyses. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250 MHz. Mass spectra were recorded on a Varian MAR 311A double focussing mass spectrometer. Melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. Microanalyses were performed by the University Analytical Center, Tucson, AZ.

Dimerization in the Solid State. A 1-mm thick layer of 217 mg (1.0 mmol) of pulverized **1** was irradiated for 16 h to give a

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[3] Harding, M. M. *Acta Crystallogr., Sect. C* **1983**, *C39*, 397. We have also solved the crystal structure of **3**, R = Me, and noted considerable extraneous electron density in the channels along the c axis. Our crystals came out of an acetone solution (open to the air) during the irradiation, but we think this electron density is due to disordered *water* rather than acetone since the ^1H NMR spectrum of such crystals shows a significant water peak but no acetone peak.

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