A Molecular Orbital Study of the Isomerization Mechanism of Diazacumulenes

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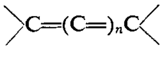
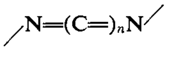
Abstract: Inversion barriers and geometries of AB_3 molecules calculated using the INDO method[3] are in satisfactory agreement with experiment. The diazacumulenes (II) with an even number of atoms are calculated to have a higher configurational stability than those with an odd number of atoms. *cis*-Diimide and *cis*-difluorodiimide should be more stable thermodynamically than the corresponding *trans* isomers. The configurational stability of carbodiimide is predicted to be low (comparable to that of ammonia), the isomerization being a combination of rotation and inversion. However, difluorocarbodiimide should be stable enough to permit resolution.

The stereoisomerization of cumulenes (I) is believed to involve a rotation about the double bonds. This type of mechanism would explain the relatively high configurational stabilities observed.[4,5] If the end atoms in the cumulenes are replaced by nitrogens, an additional mode of stereoisomerization is conceivable, namely the inversion on the nitrogens. If the inversion mechanism predominates, one would expect the isomerization energy to be considerably lower than that associated with a rotation about the double bonds. This might preclude the possibility of isolating stereoisomers of the diazacumulenes.


I, $n = 0, 1, \ldots$


II, $n = 0, 1, \ldots$

Azo compounds are the first members of the series II ($n = 0$), and it is well known that some of them do exist as *cis–trans* isomers. Apart from aromatic azo compounds,[6] there should be mentioned *cis*- and *trans*-difluorodiimide[7,8] whose *trans*- to *cis*-activation energy has been found to be 32.2 kcal/mole.[9] The chemistry of carbodiimides (II, $n = 1$) has been studied extensively.[10] The dipole moments found for certain diarylcarbodiimides[11] confirm the structure to be expected from a simple valence theory: the N–C–N chain is linear and the substituents lie approximately in two mutually perpendicular planes. Exact structure determinations are lacking, however. Carbodiimides, like allenes, are expected to exhibit optical activity. There have been a number of unsuccessful attempts to resolve carbodiimides.[12,13] Quite recently Schlögl, *et al.*,[14] claimed to have achieved partial resolution of diferrocenylcarbodiimide. These results indicate a low activation energy for the stereoisomerization. It is, therefore, apparent that the stereochemical stabilities of the first two members of the diazacumulene series are quite different. Consequently, we thought it worthwhile to gain some theoretical insight into the mechanism and activation energies of this isomerization. The semiempirical SCF–MO method (CNDO) recently elaborated by Pople, *et al.*,[15–17] seemed particularly useful for this purpose. It includes all valence electrons and yet is simple enough to permit the calculation of the equilibrium geometry of large molecules. A number of AB_3 molecules with known experimental data were studied first in order to estimate the reliability of our calculations.

Method of Calculation

The principal features of the CNDO method are as follows: (1) use of Slater-type orbitals (STO)

$$\phi_\mu(x,y,z) = \phi_\mu(\mathbf{x}) \quad \mu = 1, 2, \ldots$$

as basis; (2) explicit inclusion of all valence electrons; (3) simplification of Roothaan's[18] full LCAO-SCF procedure by complete neglect of differential overlap, *i.e.*, we put

$$S_{\mu\nu} = \int \phi_\mu(\mathbf{x})\phi_\nu(\mathbf{x})\,d\mathbf{x} = \delta_{\mu\nu} = \begin{cases} 0 \text{ for } \mu \neq \nu \\ 1 \text{ for } \mu = \nu \end{cases}$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu(\mathbf{x}_1)\phi_\nu(\mathbf{x}_1)\frac{1}{r_{12}}\phi_\lambda(\mathbf{x}_2)\phi_\sigma(\mathbf{x}_2)\,d\mathbf{x}_1 d\mathbf{x}_2 = \delta_{\mu\nu}\delta_{\lambda\sigma}\gamma_{AB}$$

where $\gamma_{AB} = (s_A s_A|s_B s_B)$, s_A, s_B being Slater's orbitals on atoms A and B, respectively (thus all integrals $S_{\mu\nu}$ and $(\mu\nu|\lambda\sigma)$ are neglected unless $\mu = \nu$ and $\lambda = \sigma$, and the latter integrals depend only on the atoms on which orbitals ϕ_μ and ϕ_λ are centered); (4) use of two semiempirical parameters per atom of the first row of the periodic table.

Inversion barriers for AB_3 molecules calculated using the CNDO method turned out to be too high; however, much better agreement with experiment was obtained

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[3] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

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when the INDO method was used. Therefore, the INDO method was adopted for all our calculations. INDO (intermediate neglect of differential overlap) differs from CNDO in the one-center integrals $(\mu\nu|\mu\nu)$ in which ϕ_μ and ϕ_ν are both on atom A. In INDO, these one-center integrals are retained explicitly, but in all other respects, CNDO and INDO are identical. The energies of triplet states were calculated using the INDO unrestricted Hartree–Fock scheme,[3] *i.e.*, allowing electrons with α and β spin to occupy different orbitals.

The bond lengths and bond angles of all species were minimized with respect to energy. All calculations were performed on the CDC 1604 computer at Mellon Institute using a FORTRAN 63 program. As an example for the amount of time required, a complete minimization of the energy with respect to geometry took 35 min for singlet *cis*-1,2-difluorodiimide and 65 min for triplet *cis*-1,2-difluorodiimide. The input required consisted of the atomic numbers of all atoms, an initial set of bond lengths, bond angles, and dihedral angles, and the total charge and multiplicity.

Results and Discussion

1. AB_3 Molecules. In Table I our results are compared with the corresponding experimental quantities. The inversion barriers were taken to be the difference in energy between the pyramidal form and planar transition state. The A–B bond lengths in the transition states were those giving the lowest energies.

Table I. Comparison of Experimental and Calculated Geometries and Inversion Barriers for AB_3 Molecules

Molecule	Valence angle, deg		Bond length, Å		Inversion barrier, kcal/mole	
	Theory	Exptl	Theory	Exptl	Theory	Exptl
CH_3^+	120	120	1.12	...	0	0
CH_3^-	104.1	...	1.14	...	15.4	16–18[a]
NH_3	106.4	109.1[b]	1.07	1.019[b]	8.8	5.8[e]
NF_3	104.2	102.2[c]	1.25	1.371[c]	62.6	56–59[f]
OH_3^+	117.8	115–117[d]	1.05	1.02[d]	0.1	1.7[g]

[a] See text. [b] O. Bastiansen and B. Beagley, *Acta Chem. Scand.*, **18**, 2077 (1964). [c] J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950). [d] R. Savoie and P. A. Giguère, *J. Chem. Phys.*, **41**, 2698 (1964). [e] J. D. Swalen and J. A. Ibers, *ibid.*, **36**, 1914 (1962). [f] This value was communicated to us by Koeppl, *et al.*, as a correction to the value quoted in footnote *g*. [g] G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).

CH_3^+. There are no direct experimental observations on CH_3^+; however, carbonium ions in general are believed to be planar. A Gaussian calculation by Csizmadia[19] on CH_3^+ gave a planar structure. In addition, one would expect this molecule to be planar on the basis of Walsh's rules.

CH_3^-. No experimental results are available for CH_3^- itself. Concerning carbanions in general, Cram, *et al.*,[20] found inversion barriers of 16 to 18 kcal/mole for sulfonyl carbanions in DMSO. This agrees quite well with the INDO result; however, barriers for ions obtained in solution are not directly comparable to the calculated barriers. The solvent may well stabilize a pyramidal configuration of the anion, and in addition the carbanions may not be completely free. Thus Cram *et al.*, explain the inversion of the sulfonyl carbanions as being due to ion-pair dissociation. Similar considerations may apply to other carbanions in solution.[21] An X-ray diffraction study of the tricyano carbanion, $(CN)_3C^-$, shows it to be slightly pyramidal,[22] although in this case one might have expected a planar structure due to resonance interaction of the CN groups. This would indicate that replacing the CN groups by hydrogens might make the molecule more strongly pyramidal. Walsh's rules favor a nonplanar structure, CH_3^- having the same number of electrons as ammonia. A calculation by Hartmann, *et al.*,[23] which treats the central atom as a pseudo-Ne atom and the three protons as a perturbation yields a valence angle of 90.8°. On the other hand, a one-center expansion calculation by Rutledge[24] using STO's gave a planar structure for CH_3^-.

OH_3^+. The geometry calculated is in satisfactory agreement with the experimentally determined structure. The inversion barrier seems to be unknown; Bishop[25] has calculated a value of 0.5 kcal/mole using a nine-term, single-center molecular wave function composed of STO's having noninteger principal quantum numbers. This is in fair agreement with our calculation. Costain and Sutherland[26] have devised a method which allows the calculation of the inversion barrier of pyramidal AB_3 molecules from two infrared frequencies (the symmetric bend and symmetric stretch) or from the corresponding force constants. The potential energy is expressed as

$$V = \frac{3}{2} K_l(\Delta l)^2 + \frac{3}{2} K_\delta(\Delta\alpha)^2$$

where K_l and K_δ are the symmetric stretching and bending force constants, respectively, Δl is the change in each bond length, and $\Delta\alpha$ is the change in each bond angle. Using this technique Koeppl, *et al.*,[27] have calculated inversion barriers for a large number of AB_3 molecules. Their result for OH_3^+ was 1.7 kcal/mole. This agrees with our prediction that this barrier should be small.

NH_3. The valence angle and inversion barrier calculated are in satisfactory agreement with the experimental values. The NH bond is slightly too long.

NF_3. Again the valence angle agrees well with experiment; however, the calculated NF bond length is well below the observed value. The inversion barrier of NF_3 is not known with certainty. Berry[28] estimates the rate of tunneling of NF_3 to be comparable to that of AsH_3, the inversion barrier of the latter being approximately 35 kcal/mole. The barrier calculated by Koeppl, *et al.*, is 56–59 kcal/mole,[29] in very good agreement with our results.

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(26) C. C. Costain and B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

(27) See footnote, Table I.

(28) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(29) See footnote, Table I.

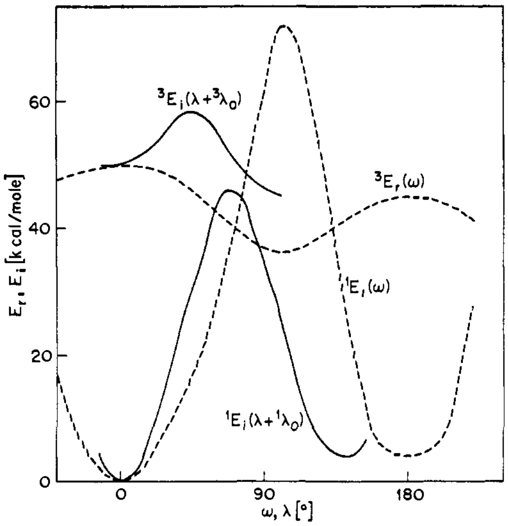
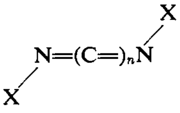


Figure 1. Singlet and triplet potential curves for diimide: E_i $(\lambda + \lambda_0)$, inversion on one nitrogen, λ_0 being the valence angle in *cis*-diimide; $E_r(\omega)$, rotation about the double bond.

2. Diazacumulenes. Three different mechanisms of isomerization were considered: the inversion on one nitrogen, the rotation about the double bonds, and the inversion on both nitrogens simultaneously. The latter mechanism was always found to involve much higher activation energies than the first two (see Figures 2–7). Five basic geometries (III to VII) were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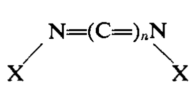
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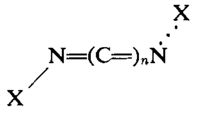
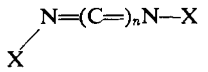

V (dihedral angle ω = 90°)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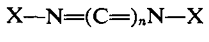
VII

considered for the diazacumulenes. To obtain the potential curve $E_i(\lambda)$ for inversion on one nitrogen, we minimized the energy with respect to bond lengths and the second valence angle at various values of λ. The dihedral angle ω was kept constant in this case. Similarly the potential curve $E_r(\omega)$ for rotation was obtained by minimizing the energy with respect to bond length and valence angles at several different values of the dihedral angle ω. C_2 symmetry was always maintained during this minimization. In most cases it was sufficient to evaluate the function $E_i(\lambda)$ in the neighborhood of III, IV, and VI and $E_r(\omega)$ in the neighborhood of III, IV, and V. This procedure was applied to both the lowest singlet state and the lowest triplet state.

Diimides. From Figures 1 to 3 it can be seen that the *cis*- and *trans*-diimides (III and IV, $n = 0$) represent stable compounds. For both diimides the *cis* form is found to be thermodynamically more stable than the *trans* form. The energy difference for the difluoro species (4.1 kcal/mole) is in good agreement with the value of 3.0 kcal/mole found by Armstrong and Marantz[8] from equilibrium measurements. The corresponding energy difference calculated for diimide is 4.5 kcal/mole; however, no experimental measurements are available. The existence of both *cis*- and *trans*-diimide has been established spectroscopically.[30] A calculation by Alster and Burnelle[31] using Hoffmann's extended Hückel theory[32] predicts *cis*-diimide to be more stable than *trans* by 8.5 kcal/mole. We have not been able to partition the total energy of the diimides in such a way as to make the relative energies of the *cis* and *trans* isomers easily explainable.

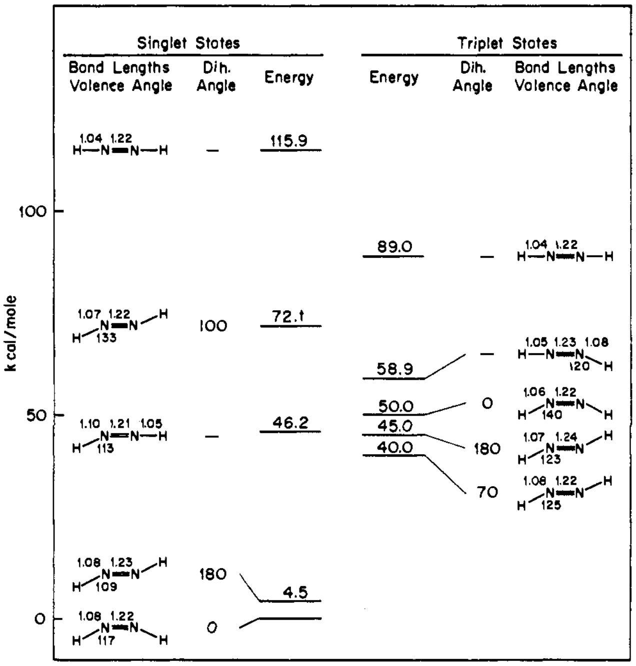

Figure 2. Energies and geometries for various states of diimide.

As to the mechanism of isomerization, the following conclusions may be drawn from Figure 1. If only singlet states are involved, an inversion on one nitrogen is calculated to require an activation energy of 46 kcal/mole [$^1E_i(\lambda + {}^1\lambda_0)$ curve, $^1\lambda_0$ being the equilibrium valence angle in singlet *cis*-diimide], while rotation would require an activation energy of 72 kcal/mole [$^1E_r(\omega)$ curve]. Thus singlet isomerizations should proceed through an inversion on one nitrogen. If triplet states are involved in the isomerization, then the inversion on nitrogen is not a likely mechanism because the triplet potential curve for inversion, ^3E_i, does not cross the singlet potential curve for inversion ^1E_i. Since the triplet and singlet potential curves for rotation, ^3E_r and ^1E_r, do have a crossing point, one must conclude that a triplet isomerization proceeds by a rotation around the double bond. The activation energy in this case would be 40 kcal/mole. A theoretical prediction as to whether a singlet or triplet mechanism in a particular *cis–trans* isomerization prevails cannot be made. Experimentally singlet mechanisms are usually indicated by a large preexponential factor in the expression for the rate constant. An almost identical diagram results for difluorodiimide. The calculated singlet and triplet activation energies are 68 and 52 kcal/mole, respectively. These results suggest a relatively high configurational stability for both diimides. In Figures 2 and 3 the energies and geometries of the various states of the diimides are shown. It is interesting to note that for both diimides the dihedral angle of the transition states for rotation deviates from 90°.

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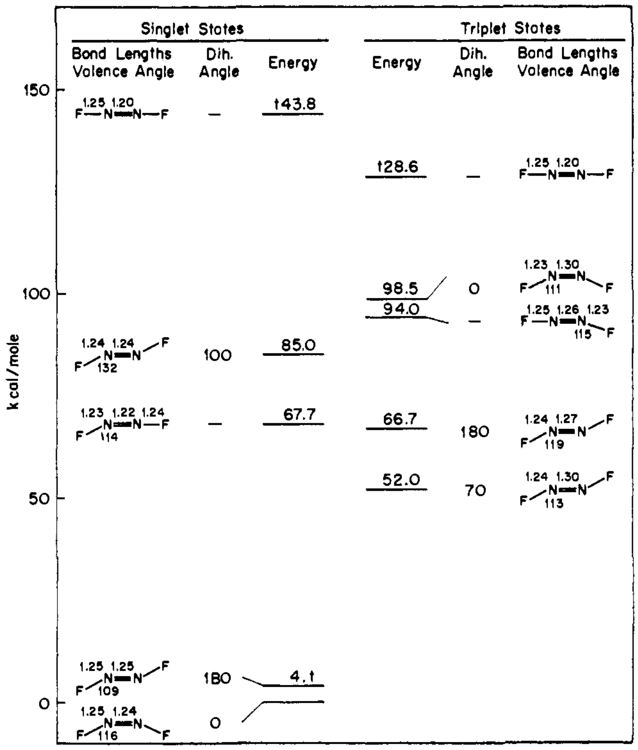

Figure 3. Energies and geometries for various states of difluorodiimide.

The *cis*-to-*trans* isomerization of difluorodiimide has been shown to proceed through a singlet transition state with an activation energy of 35.2 kcal/mole.[9] Although this is well below our calculated value, the high configurational stability predicted by our calculation is definitely borne out by experiment. The calculation by Alster and Burnelle[31] on diimide also suggests that the isomerization involves inversion on nitrogen, but they find an activation energy for the *trans*-to-*cis* isomerization of only 3.1 kcal/mole. This would preclude any possibility of isolating *cis*- and *trans*-diimide in a pure state.

Kuczkowski and Wilson[33] have determined the structure of *cis*-difluorodiimide by microwave analysis. Their values of R_{NN} = 1.214 Å and $\angle$NNH = 114.5° agree quite well with our calculated values; however, the value of R_{NF} = 1.25 Å given by INDO is again much shorter than the observed (1.348 Å). No similar structure determinations are available for *trans*-difluorodiimide, but here again one would expect our N–F distance to be too short. Our prediction of quite different NNF bond angles for *cis*- and *trans*-difluorodiimide seems reasonable on the basis of greater nonbonded repulsion in the *cis* form. Noggle, *et al.*,[34] have predicted a large difference in the angles of the two species on the basis of indirect N–F coupling constants for the *cis* and *trans* forms. Although no structural information is available for diimide, our results seem reasonable when compared with N_2F_2.

Carbodiimides. The unsubstituted carbodiimide exists only in the form of its isomer, cyanamide. No attempts to prepare difluorocarbodiimide have been reported.

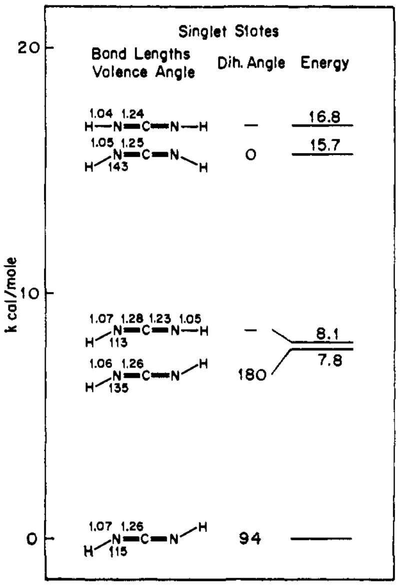

Figure 4. Energies and geometries of various states of of carbodiimide.

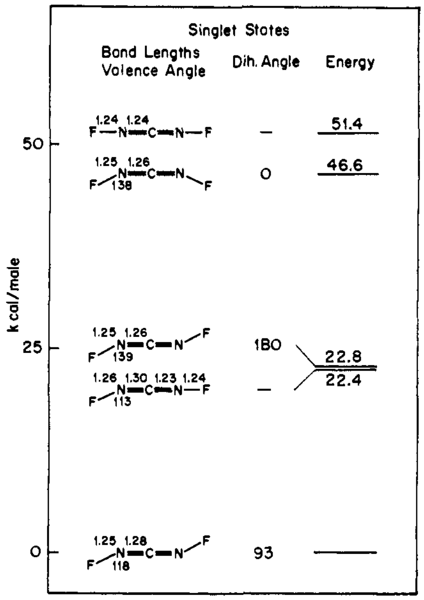

Figure 5. Energies and geometries of various states of difluorocarbodiimide.

Our results are presented in Figures 4 and 5. The thermodynamically most stable forms of the carbodiimides are found to have the substituents in two almost perpendicular planes (V, *n* = 1), the dihedral angles being 94 and 93° for carbodiimide and difluorocarbodiimide, respectively. The CN bond lengths and the bond angles seem reasonable, while the NH bond length is probably too high and the NF bond length is too low. No experimental structure determinations on any carbodiimide are available.

We find that the lowest transition state for the stereoisomerization of carbodiimide is only about 8 kcal/mole above the normal state. The configurational stability should thus be comparable to ammonia. It would, therefore, seem that attempts to prepare optically active carbodiimides will meet with the same difficulties as were encountered with optically active

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[33] P. L. Kuczkowski and E. B. Wilson, Jr., *J. Chem. Phys.*, 39, 1030 (1963).

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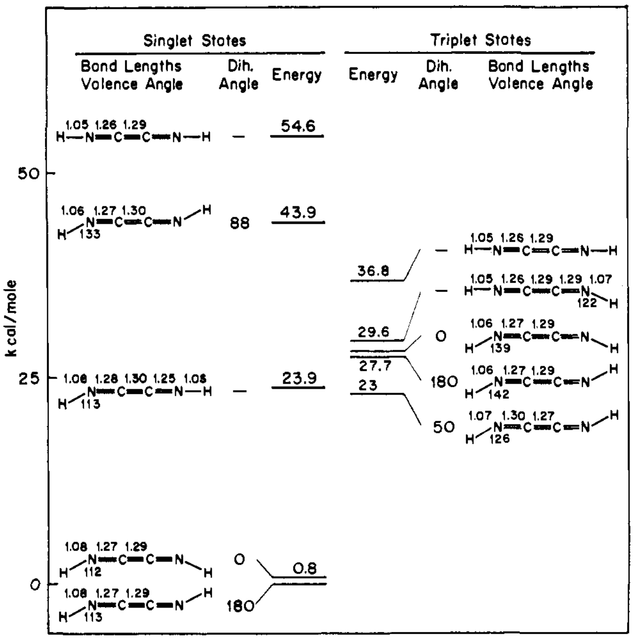

Figure 6. Energies and geometries of various states of diazabutatriene.

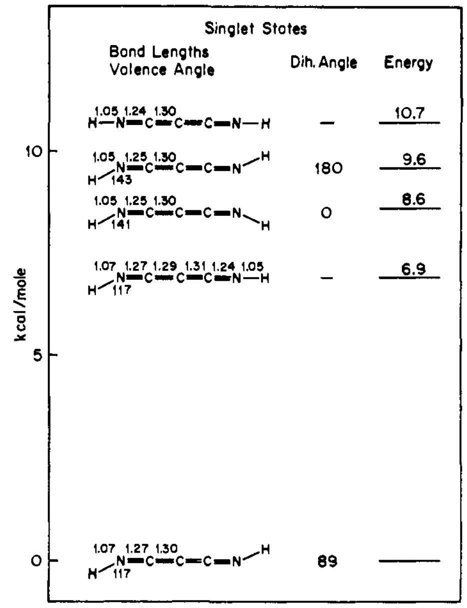

Figure 7. Energies and geometries of various states of diazapentatetraene.

amines. On the other hand, difluorocarbodiimide is predicted to have a sufficiently high configurational stability to permit its resolution into optically active species, the activation energy for the isomerization being 22.4 kcal/mole. This result is not surprising in view of the high inversion barrier of NF_3 as opposed to NH_3.

Our calculation slightly favors rotation through the *trans* configuration over inversion for the isomerization of the carbodiimides. The energy increases to the values given in the preceding paragraph when the dihedral angle in V ($n = 1$) is increased from 94 to 180° (rotating the substituents away from each other). At the same time the valence angle increases by about 20°. A greater energy increase is observed when the dihedral angle is decreased from 93 to 0° (rotating the substituents toward each other). Again the valence angle opens up by about 20°. The barrier for the rotation through a *cis* configuration would be 15.7 and 46.6 kcal/mole for carbodiimide and difluorocarbodiimide, respectively. The transition state for inversion on one of the nitrogens (VI, $n = 1$) is only about 0.3 kcal/mole higher in energy than that of rotation through the *trans* configuration (for both carbodiimides). Therefore, both rotation and inversion may be responsible for the isomerization of the carbodiimides. A combination of inversion and rotation is also indicated by the large opening of the valence angle in the *trans* form, since a pure rotation would involve at most a much smaller change in angle. The lowest triplet transition states for both carbodiimides are found to be some 60 kcal/mole higher than the normal states; thus it appears that triplet mechanisms can be ruled out for the isomerization of carbodiimides.

Diazabutatriene. The energy difference between *cis* and *trans* (III and IV, $n = 2$) is found to be negligible, *trans* being slightly favored (see Figure 6). The configurational stability is predicted to be much higher than that of carbodiimide, the next lower member of the series. The calculated activation energy for the isomerization through a singlet transition state is 23.9 kcal/mole. This would allow the isolation of *cis* and *trans* isomeric diazabutatrienes. As for the diimides, the isomerization by a singlet mechanism should involve an inversion on nitrogen while a rotation should be responsible for the isomerization by way of a triplet mechanism.

Apart from the NH bond length, the calculated geometries seem reasonable. The central CC bond in butatriene has been measured[35] to have a length of 1.28 Å which compares favorably with our calculated value for the rather similar bond in diazabutatriene.

Diazapentatetraene. The calculated activation energy of 6.9 kcal/mole for the isomerization is significantly lower than that of diazabutatriene (see Figure 7). Thus with respect to configurational stability the diazacumulenes fall into two distinct series. The members with an even number of atoms have a much higher configurational stability than those with an odd number of atoms (see Table II). The energies of all the transition states for the isomerization of diazapentatetraene are quite close to one another. Again a combination of inversion and rotation is indicated for the isomerization process. The lowest triplet transition state for the diazapenta-

Table II. Calculated Activation Energies for the Isomerization of Diazacumulenes, Assuming Singlet Transition States

$\mathrm{H{-}N{=}(C{=})_nN{-}H}$	Activation energy, kcal/mole
0	46.2
1	8.0
2	23.9
3	6.9

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[35] O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, **15**, 1557 (1961).

tetraene isomerization was found to be some 40 kcal/mole above the normal state, so triplet mechanisms should be unimportant.

It should be noted that for the species V ($n = 0$ and 2) there are two degenerate singlet configurations. It is possible therefore, that configuration interaction may lower the energy of the singlet transition state for rotation. This energy lowering would have to be about 20 kcal/mole to affect our conclusions concerning the mechanism of isomerization for these molecules.

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The Monomer Distributions of Propylene Oxide–Maleic Anhydride Copolymers

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Abstract: The monomer distributions in the copolymer propylene oxide–maleic anhydride (PO–MA) prepared by two different homogeneous catalysts have been determined. Gas chromatographic techniques which accurately determine the relative concentrations of runs of propylene oxide up to length 11 have been employed to make the direct demonstration of the suitability of Markoffian statistics in describing the monomer distribution in low-conversion PO–MA copolymers. Analysis of the monomer distribution in high-conversion PO–MA copolymers indicates that the observed distribution may be a sum of two different distributions, each of which is Markoffian. This result is interpreted in terms of a chemical modification of the catalyst during the copolymerization.

A recent study of the monomer distribution in the copolymer propylene oxide–maleic anhydride (PO–MA), $\text{—C(=O)CH=CHC(=O)O(CHCH}_3\text{CH}_2\text{O—)}_N$, polymerized by various homogeneous catalysts, was performed by a nuclear magnetic resonance (nmr) analysis of the copolymer and a gas–liquid partition chromatographic (glpc) analysis of the glycol ethers obtained from hydrolysis of the copolymer.[1] The main conclusion of this study was that high-order Markoffian statistical descriptions of the monomer distributions fitted the observed glpc, nmr, and composition data for all catalyst systems investigated.

This paper describes the results obtained from analysis of PO–MA copolymers by an improved glpc technique. By using volatile derivatives of the glycol ethers obtained from hydrolysis of the copolymer, the relative numbers of runs of PO up to a length of 11 can be determined accurately. The previous glpc method only permitted detection of runs of PO up to a length of four and only up to a length of three with any accuracy. The present values for the shorter runs are in agreement with the previously reported experimental results. The relative concentrations of the longer runs in *low*-conversion copolymers confirm the conclusion that high-order Markoffian statistics are applicable to PO–MA monomer distributions. The relative concentrations of the longer runs of PO in *high*-conversion copolymers indicate that, within both $SnCl_4$ and $SbCl_5$ catalysts systems, at least two distinctly different catalyst types, each with a third-order Markoffian memory, may be generating copolymer chains.

Experimental Section

Glpc analysis was performed on an F & M Model 720 chromatograph operated with an injection port temperature of 300°, detector block temperature of 300°, flow rate of 185 ml/min, and bridge current of 150 mA. Response factors for the trimethylsilyl ether derivatives of the monomer, dimer, trimer, tetramer, pentamer, and hexamer of propylene glycol were obtained as follows. Monomer, dimer, and trimer glycols were obtained from commercial sources. Tetramer, pentamer, and hexamer were isolated from a synthetic glycol mixture on a 0.25 in. o.d. by 3-ft 2% SE-52 on 60–80 mesh gas pack F analytical glpc column programmed from 130 to 300° at the rate of 10°/min. Synthetic blends of the monomer through hexamer at various concentrations were made, and 20 mg of tetraethylene glycol dimethyl ether, used as an internal reference, was added to 100 mg of each blend. Volatile trimethylsilyl ether derivatives were formed by adding 50 μl of bis(trimethylsilyl)acetamide to 20 μl of each blend and allowing the mixtures to stand overnight at room temperature. (At least 4 hr is necessary to convert quantitatively all glycols up through the dodecamer to the corresponding trimethylsilyl ether derivative.) Ether derivatives were analyzed on a 0.25 in. × 6 ft 5% SE-33 on 60–80 mesh Diatoport-S column programmed from 75 to 350° at the rate of 7.5°/min. A calibration curve for each glycol was made by plotting the ratio of glycol peak area to internal standard peak area against mole per cent glycol. The slope of the line (extrapolated through zero) gave the relative response factor for each glycol.

Propylene oxide–maleic anhydride copolymers were prepared using two different homogeneous catalysts, $SbCl_5$ and $SnCl_4$. Procedures for the copolymerization and hydrolysis have been given earlier.[1] The glycol ethers resulting from hydrolysis of the copolymers were derivatized and analyzed as above.

The 60-Mc/sec nmr spectra were obtained from a 15% by weight solution in $CDCl_3$ using a Varian A-60 spectrometer with an operating probe temperature of 35°.

Results

The 60-Mc/sec spectra of PO–MA copolymers prepared by two different homogeneous catalysts are pre-

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(1) R. J. Kern and J. Schaefer, *J. Am. Chem. Soc.*, **89**, 6 (1967).