

with those in the spectrum of the equimolar mixture (see footnote a to Table I for assignments) then points clearly to the contributions from  $\text{Cr}^{III}\text{Cl}_6$  and  $\text{Mo}^{III}\text{Cl}_6$  chromophores in the spectrum of  $\text{CrMoCl}_9^{3-}$ . This information makes it equally clear that reaction 3 involves electron transfer. Furthermore, the electronic spectrum of  $\text{CrMoCl}_9^{3-}$  is in full accord with a confacial, biotetrahedral structure since this structure is the only one which will simultaneously accommodate both  $\text{Cr}^{III}\text{Cl}_6$  and  $\text{Mo}^{III}\text{Cl}_6$  chromophores. Finally, the magnetic moment per formula unit of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{CrMoCl}_9$  is 4.38 BM at 295°K and 3.10 BM at 77°K. These results are in accord with antiferromagnetic coupling between the two  $S = 3/2$  spin systems.

The only other dinuclear or polynuclear species containing both chromium and molybdenum is the Cr(II)-Mo(II)-acetate compound,  $\text{CrMo}(\text{OAc})_4$ , which was recently prepared.<sup>6</sup>

**Acknowledgment.** Financial aid from the National Science Foundation (Grant No. GP-30544X) is acknowledged.

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M. S. Matson, R. A. D. Wentworth\*

Contribution No. 2550

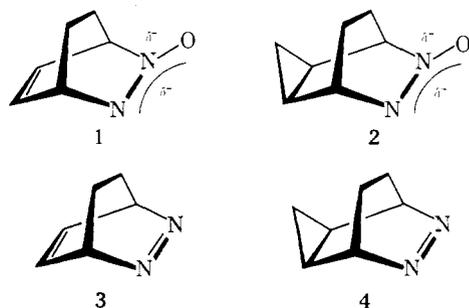
Department of Chemistry, Indiana University  
Bloomington, Indiana 47401

Received September 10, 1974

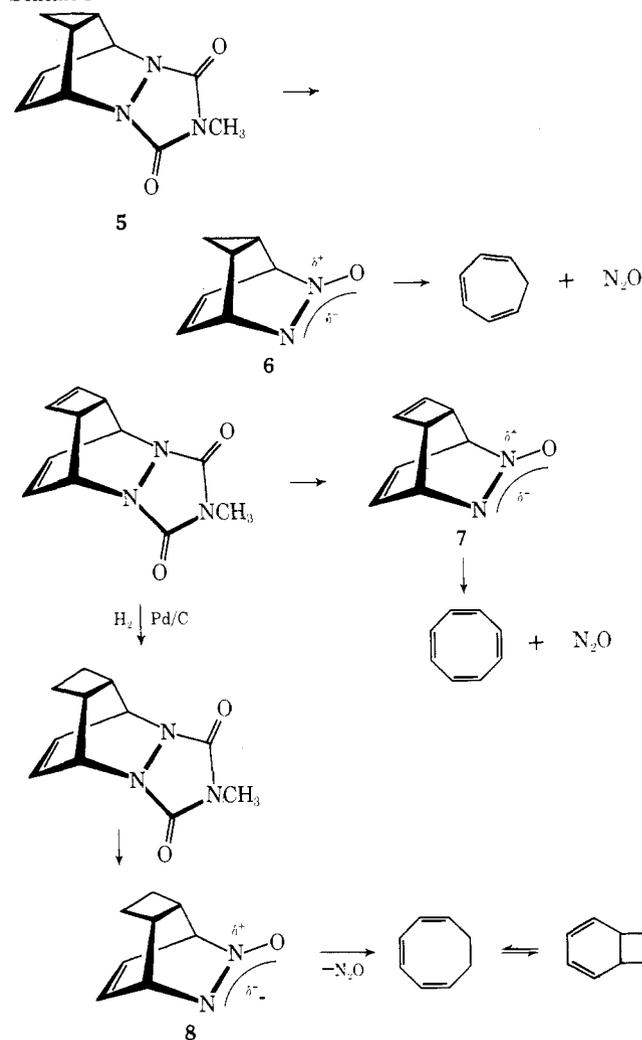
### *cis*-Azoxyalkanes. V. Concerted Retrocycloaddition of $\text{N}_2\text{O}^1$

Sir:

Pericyclic processes characterized by high symmetry proceed in a relatively well-defined manner.<sup>2</sup> Removal of symmetry by the introduction of strong perturbations, however, may possibly affect both the stereochemistry<sup>3</sup> and the energetics<sup>4</sup> of a concerted reaction. Few asymmetric but formally pericyclic transformations have been unambiguously demonstrated to take place without the intervention of intermediates.<sup>5</sup> Consider the retrocycloaddition of heterocycles 1-4. The thermal stability of *N*-oxides 1 and 2 stands in stark contrast to that of the corresponding azo analogs 3 and 4. A lower limit of  $10^6$  has been placed on the relative rate of nitrogen extrusion *vs.* the corresponding loss of nitrous oxide.<sup>6</sup> The azo compounds are believed to eject molecular nitrogen by way of a single concerted step.<sup>7</sup> *A priori*



Scheme I



several pathways exist for the analogous *cis*-azo-*N*-oxide system. We now wish to present evidence that the thermolysis of highly condensed azoxy alkanes is likewise concerted. The analogy between the azo and the azoxy series extends to the participation of cyclopropane and cyclobutane rings in the transition state for fragmentation.

As previous we have taken advantage of the great stability of azo-*N*-oxides to prepare several new systems with hydrocarbon backbones inaccessible in the azo series.<sup>8</sup> Hydrolytic oxidation of cycloadduct 5 with strongly basic hydrogen peroxide<sup>1,6</sup> generates compound 6 (mp 48-50°, 50% yield) in a single step.<sup>9</sup> *N*-Oxides 7 (mp 101-102°, 65%) and 8 (mp 119-120°, 80%) arise similarly as outlined in Scheme I.

Bicycle 6 decomposes quantitatively and exclusively to cycloheptatriene at temperatures slightly above ambient. First-order rates of decomposition were determined by measuring the change in absorption at 275 nm in the temperature range 30-60° ( $k_{\text{CCl}_4} = 1.66 \times 10^{-4} \text{ sec}^{-1}$  (39.4°)). The *N*-oxides 1, 7, and 8 are completely stable at 30° and require temperatures more than 100° higher for conveniently monitored rates of decomposition. In nitrobenzene (131.6°) compounds 7 and 8 deliver cyclooctatetraene and 1,3,5-cyclooctatriene,<sup>10</sup> respectively, in quantitative yield. Azoxy 1 gives rise to both cyclohexadiene and benzene. Control experiments demonstrate the latter to be a secondary product derived from oxidation of the primary diene product.<sup>11</sup> First-order rate constants were determined in nitrobenzene by periodic integration of appropriate disappearing azoxy protons against the methyl protons of anisole

**Table I.** Thermolysis Rates for Unsaturated Azoxyalkanes, 131.6°

Compd	Solvent	$10^4k$ , sec <sup>-1</sup> <sup>a</sup>	Relative rate	$\Delta G^*$ , kcal/mol
6	CCl <sub>4</sub>	$2.5 \times 10^{4b}$	$1.3 \times 10^6$	23.2
7	C <sub>6</sub> D <sub>5</sub> NO <sub>2</sub>	3.0	150	30.5
8	"	1.1	60	31.3
1	"	$2.0 \times 10^{-2}$	1.0	34.5

<sup>a</sup> Error limits are 0.06–0.17 and are standard deviations from least-squares analysis. <sup>b</sup> Extrapolated from data at lower temperatures, (cf. Table II).

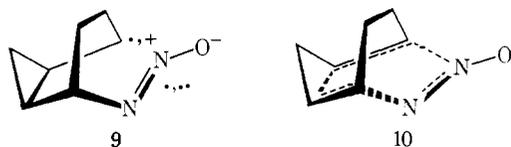
**Table II.** The Effect of Solvent on the Fragmentation of Azoxy 6

Solvent	$E_t$ value <sup>a</sup>	Rel rate <sup>b</sup>	$\Delta G^*$ , kcal/ mol <sup>b</sup>	$\Delta H^*$ , kcal/mol <sup>c</sup>	$\Delta S^*$ , eu <sup>c</sup>
<i>n</i> -Hexane	30.9	5.4	23.3		
CCl <sub>4</sub>	32.5	4.7	23.4	$25.7 \pm 0.3$	$6.2 \pm 1.0$
Dioxane	36.0	2.2	23.9		
DMF	43.8	1.2	24.3		
CH <sub>3</sub> CN	46.0	1.0	24.4		
Absolute EtOH	51.9	1.0	24.4	$23.2 \pm 0.5$	$-4.2 \pm 1.6$

<sup>a</sup> K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963). <sup>b</sup> Determined at  $52.0 \pm 0.1^\circ$ . <sup>c</sup> At  $25^\circ$ .

as internal standard. The results are given in Table I.

Aside from a synchronous process with varying degrees of timing, fragmentation of the azo-*N*-oxides by stepwise cleavage of the C–N(O) and CN bonds is the mechanistic alternative which deserves serious consideration. Homolytic and heterolytic fission correspond to diradical and zwitterionic intermediates, respectively, *i.e.*, structure **9**. A striking feature of the data in Table I is that the decomposition of **6** is accelerated over that of **1** by  $10^6$  ( $\Delta\Delta G^* = 11.3$  kcal/mol). Recent investigations indicate that the cyclopropyl group is ineffective at stabilizing an adjacent radical center<sup>12</sup> but is the most efficient unsubstituted hydrocarbon neighboring group for stabilizing a carbocation.<sup>13</sup> The  $10^6$  rate factor is thus not accommodated readily by the diradical hypothesis, **9** (+,·). Discrimination between a concerted and a zwitterionic mechanism can be inferred from a comparison of cyclopropyl *N*-oxide, **2**, and the unsaturated bicycle **1**. Compound **2** resists change for 3 hr at  $175^\circ$  (C<sub>6</sub>D<sub>5</sub>NO<sub>2</sub>), while **1** has a half-life under the same conditions of 80 min. A transition state leading to a charge separated intermediate **9** (+,·) is rendered unlikely.



Further insight into the mechanism of N<sub>2</sub>O loss is gained by considering the dependence of reaction rate on solvent polarity. For azoxy **6** the decomposition rate drops slightly as solvent polarity increases (Table II). The rate constant ratio  $k(\text{acetonitrile})/k(\text{hexane}) = 0.19$  can be compared with  $k(\text{acetonitrile})/k(\text{cyclohexane}) = 2600\text{--}29,000$  for the addition of tetracyanoethylene to enol ethers.<sup>14</sup> Zwitterionic intermediates provide the best description for the latter reaction but are again incompatible with the former.<sup>15</sup>

Both the solvent dependence and the relative rate data are consistent only with a concerted retrocycloaddition of N<sub>2</sub>O. Nonetheless activation parameters for **6** in solvents of widely different polarity (CCl<sub>4</sub>, absolute EtOH, Table II) may be interpreted in terms of a transition state somewhat

more polar than the ground state.<sup>17</sup> Consequently we picture the breakdown as in **10** whereby the CN(O) bond cleaves slightly ahead of the CN bond and leads to an increase in dipole moment.

The relative fragmentation rates of azoxy alkanes **1** and **6** leave little doubt as to the marked ability of a cyclopropyl group to assist CN bond rupture under conditions of concert. This phenomenon is well established in the azo series.<sup>7a,c,18</sup> Considerably less evidence exists for the similar participation of the cyclobutane ring,<sup>19</sup> although two of the three criteria appear to be met in certain cases.<sup>7c,20</sup> Azoxy series **1**, **6**, **7**, and **8** is unique in that each compound contains an appropriate double bond which provides assurance that decomposition be concerted. Subsequent fusion of rings allows additional effects to be measured. As for the azo derivatives the cyclobutyl cases **7** and **8** are considerably less reactive than the cyclopropane **6** ( $\Delta\Delta G^* = 7.3\text{--}8.1$  kcal/mol), but somewhat more reactive than unsubstituted **1** ( $\Delta\Delta G^* = 3.2\text{--}4.0$  kcal/mol). Most important, the relative rates of **7**, **8**, and **1** are consistent with four-ring rupture simultaneous with N<sub>2</sub>O expulsion.<sup>21</sup> Whether the small rate increment is due to strain, electronic factors, or both has yet to be ascertained.

Finally a comparison between azo-**3** and azoxy-**1** is instructive. By using reasonable activation values<sup>22</sup> the  $k(\text{azo})/k(\text{azoxy})$  destruction ratio must be revised upward to  $\geq 10^{16}$  ( $25^\circ$ ). The corresponding  $\Delta E_a \geq 26$  kcal/mol is remarkably large for two similar concerted processes different formally only by the *N*-oxide perturbation. We are exploring further the reasons behind this discrepancy.

**Acknowledgments.** The National Institutes of Health (GM-15927) generously provided partial support for the work.

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- (15) The unusual response of the TCNE–enol ether reaction to solvent polarity has been estimated to result from a  $\Delta\mu(\text{transition state} - \text{ground state}) = 9.1\text{--}12.0$  D.<sup>14</sup> As a consequence of the polarity of the *N*-oxides **1** and **6–8**, probably  $5\text{--}7$  D,<sup>16</sup> a  $\Delta\mu(\text{transition state} - \text{ground state}) = 5\text{--}7$  D can be estimated for a zwitterionic azoxy decomposition, **9** (+,·). Thus the rate variation of **9** (+,·) with solvent polarity is expected

- to be less than  $10^3$ – $10^4$ , but neither qualitatively nor quantitatively as depicted in Table II.
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Henrik Olsen, James P. Snyder\*<sup>24</sup>

Department of General and Organic Chemistry, H.C. Ørsted Institute, University of Copenhagen 2100 Copenhagen Ø, Denmark

Received August 15, 1974

### Carbon Monofluoride. Evidence for a Structure Containing an Infinite Array of Cyclohexane Boats

Sir:

Poly(carbon monofluoride,  $(\text{CF}_x)_n$ , has recently been a subject of interest in both basic<sup>1,2</sup> and applied<sup>3,4</sup> research. Many of its unique properties arise from its lamellar structure of weakly coupled nongraphitic  $\text{sp}^3$ -carbon fluorine sheets. For no compelling reason, the geometry of these layers has been assumed to be an infinite array of trans-linked cyclohexane chairs.<sup>5,6</sup> We have found that such an assignment is inconsistent with the results of nuclear magnetic resonance second moment studies and that the most plausible structure compatible with these and other experimental measurements is the infinite array of cis-trans-linked cyclohexane boats<sup>7</sup> illustrated in Figure 1.

The materials investigated were Fluorographites  $\text{CF}_x$  ( $x$

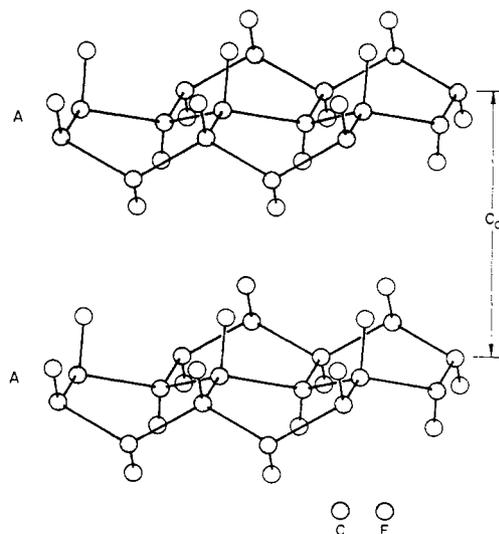


Figure 1. Structure of poly(carbon monofluoride) composed of an infinite array of cis-trans-linked cyclohexane boats.

$= 1, 1.1$ ) obtained from Ozark-Mahoning. Carbon combustion analyses yielded formulas by difference of  $\text{CF}_{1.06}$  and  $\text{CF}_{1.15}$ , respectively. The infrared spectrum (1070 (m), 1215 (s),  $1348 \text{ cm}^{-1}$  (m)) is analogous to that obtained by previous workers.<sup>1,2,6,8</sup> Powder X-ray diffraction of  $\text{CF}_{1.06}$  calibrated against silicon showed lines at 6.16, 2.05, and  $1.54 \text{ \AA}$  assignable as  $(00l)$  reflections of a lattice with  $c_0 = 6.16 \text{ \AA}$ , as well as lines at 2.21 and  $2.13 \text{ \AA}$ . Rudorff<sup>5,6</sup> has shown the  $c_0$  of  $\text{CF}_x$  to be a function of fluorine content. Recent workers have reported  $d$  values of<sup>1</sup> 5.80, 2.89, 2.22, and  $1.29 \text{ \AA}$  ( $c_0 = 5.8 \text{ \AA}$ ) and<sup>9</sup> 6.0, 2.23, and  $1.30 \text{ \AA}$  ( $c_0 = 6.0 \text{ \AA}$ ).

Structural investigations employing the nuclear magnetic resonance absorption mode second moment afford precise values of internuclear magnetic moment separations when a relatively complete knowledge of compound geometry already exists.<sup>10–14</sup> As CF is available only as a polycrystalline powder, no studies of the angular dependence of the second moment can be made, and evaluation by means of the Van Vleck<sup>10–14</sup> formula (eq 1) leads to determination of only one parameter from knowledge of the experimentally obtained polycrystalline second moment.

Table I. Theoretical Evaluation of the Second-Moment Formula (eq 1) for Infinite Boat and Chair Structures<sup>a</sup>

Boat model	Second moment (G <sup>2</sup> )	Chair model	Second moment (G <sup>2</sup> )	
			Distorted tetrahedron	Tetrahedron
	0.0088		0.0038	0.0039
	0.0538		0.0132	0.0138
	0.4669		0.0618	0.0631
	20.5082		1.2544	1.3644
	0.5527		7.5003	7.9898
	0.0538		0.7749	0.7496
	0.0094		0.0618	0.0631
			0.0112	0.0113

<sup>a</sup> Because all fluorine atoms are magnetically equivalent in either the chair or the boat form, the double sum of eq 1 reduces to a single sum, representing the interactions of one "test" fluorine nucleus with all others in the lattice. The second-moment values in the above are for interactions of the circled test fluorine with each of the nearest 1600 fluorine nuclei in the indicated fluorine plane. The sum of these contributions for the tetrahedral boat structure is  $21.7 \text{ G}^2$ . For the infinite chair structure, we have calculated second moments arising from not only a tetrahedral carbon array but also a distorted tetrahedral array which will allow indexing of the  $2.22\text{-\AA}$  diffraction line.<sup>6</sup> The values are 10.3 and  $9.7 \text{ G}^2$ , respectively.