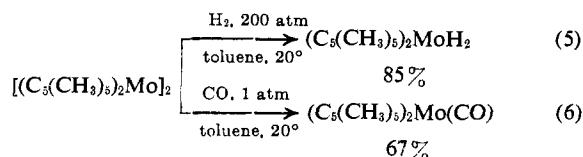


mediate  $[(C_5H_5)_2Mo]$  gives  $(C_5H_5)_2MoH_2$  in high yields.<sup>3</sup> This type of addition is similar to that occurring with  $[(C_5H_5)_2Ti]$ ,<sup>4-6</sup> another electron-deficient molecule, except that in the molybdenocene system there is no indication of a reversible formation of the metallocene by loss of  $H_2$  from the dihydride. The reactive molybdenocene monomer may be trapped also with carbon monoxide to yield a novel, bright green molybdenocene monocarbonyl,  $(C_5H_5)_2Mo(CO)$ . This compound is also obtained, although in lower yields, by a butyllithium reduction of  $(C_5H_5)_2MoCl_2$  in THF solution in the presence of CO.  $(C_5H_5)_2Mo(CO)$  is characterized by a single sharp nmr absorption at  $\tau$  5.65, a single sharp carbonyl stretching absorption at  $1905\text{ cm}^{-1}$ , and a mass spectrum with peaks at  $m/e$  258 and 230, corresponding to  $[(C_5H_5)_2Mo(CO)]^+$  and  $[(C_5H_5)_2Mo]^+$ .<sup>2</sup>

The molybdenocene intermediate also coordinates 1 equiv of  $N_2$  (eq 4). When the reduction of  $(C_5H_5)_2MoCl_2$  is performed under a pressure of 250 atm of  $N_2$ , the autoclave containing the reaction vessel cooled to  $-78^\circ$ , and the reaction mixture warmed to room temperature on a vacuum line, close to 1 mol of  $N_2$ /mol of molybdenocene is recovered. The thermal instability of this complex has thus far thwarted a structural characterization.

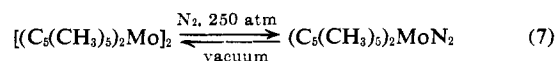
In an attempt to more fully characterize the molybdenocene system, bis(pentamethylcyclopentadienyl)molybdenum dichloride was prepared in a manner similar to that described for  $(C_5H_5)_2MoCl_2$ .<sup>7</sup> Upon sodium amalgam reduction of  $(C_5(CH_3)_5)_2MoCl_2$  under argon, a bright yellow crystalline decamethylmolybdenocene species was obtained. The mass spectrum of the compound shows its highest mass peak at  $m/e$  370 corresponding to  $[(C_5(CH_3)_5)_2Mo]^+$ . Freezing point depressions measured in benzene yield a molecular weight of 740, in accord with the presence of  $[(C_5(CH_3)_5)_2Mo]_2$  in these solutions.<sup>8</sup> The absence of a dimer peak in the mass spectrum is probably due to a weak and readily cleaved molybdenum-molybdenum bond in the decamethyl-substituted dimer.<sup>9</sup>

The reactivity of  $[(C_5(CH_3)_5)_2Mo]_2$  with  $H_2$  and CO far exceeds that of the relatively inert unsubstituted  $[(C_5H_5)_2Mo]_2$  (eq 5, 6). Both products have been fully



characterized by nmr, ir, and mass spectral data and will be described in detail in a later communication. The fact that the *in situ* reactions of the  $[(C_5H_5)_2Mo]$  intermediate are reproduced by the compound  $[(C_5-$

$(CH_3)_5)_2Mo]_2$  indicates again that the monomer  $(C_5-(CH_3)_5)_2Mo$  is relatively easily available from the dimer. The higher reactivity of  $[(C_5(CH_3)_5)_2Mo]_2$  as compared to that of  $[(C_5H_5)_2Mo]_2$  is also demonstrated in that the methyl-substituted dimer reacts reversibly with molecular nitrogen in toluene (eq 7). Even the dry crys-



talline powder of  $[(C_5(CH_3)_5)_2Mo]_2$  reacts with nitrogen at 250 atm to yield a product that evolves 1 equiv of  $N_2$ /equiv of molybdenum upon warming to room temperature under vacuum; as a solid, the nitrogen complex  $(C_5(CH_3)_5)_2MoN_2$  is somewhat more stable than in solution. Its structural characterization is presently being undertaken, together with similar studies on  $(C_5H_5)_2W$  derivatives.<sup>10, 11</sup>

The postulated intermediate  $[(C_5H_5)_2Mo]$  exhibits a striking analogy of its reaction patterns to those of a carbene. Similar observations were reported earlier for the titanium analog  $[(C_5H_5)_2Ti]$ .<sup>6</sup> The reducibility of  $N_2$  in  $(C_5H_5)_2Ti-N_2-Ti(C_5H_5)_2$  as opposed to the lack of such a reactivity in  $(C_5H_5)_2Mo-N_2$ , and the implication of these findings for the respective roles of 14- and 16-electron species in  $N_2$  reduction reactions, will be the subject of further reports.

**Acknowledgment.** These investigations were supported by a grant (GP 19421) from the National Science Foundation.

(10) The occurrence of  $(C_5H_5)_2W$  as a reaction intermediate in alkane eliminations from  $(C_5H_5)_2WHR$  has also been postulated recently by B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971).

(11)  $(C_5H_5)_2WH_2$  and the novel compounds  $(C_5H_5)_2W(CO)$  and  $[(C_5H_5)_2W]_2$  are obtained under conditions analogous to those described above: J. L. Thomas, unpublished results.

Joseph L. Thomas, Hans H. Brintzinger\*

Department of Chemistry, The University of Michigan  
Ann Arbor, Michigan 48104

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### Solvent Dependence in the Photochemical Dimerization and $[\pi 2_a + \sigma 2_a]$ Rearrangement of a Bridged 3,5-Cycloheptadienone<sup>1</sup>

Sir:

We wish to report the unique solvent-dependent competition between intramolecular  $[\pi 2_a + \sigma 2_a]$  rearrangement and intermolecular dimerization which occurs in the photochemistry of the tropone-cyclopentadiene  $[6 + 4]$  adduct **1**,<sup>2</sup> which incorporates both  $\beta, \gamma$ -unsaturated ketone and diene moieties.

Direct photolysis of  $\beta, \gamma$ -unsaturated ketones generally results in  $[1s, 3s]$  sigmatropic shifts, while sensitized photolysis of these ketones results in  $[\pi 2_a + \sigma 2_a]$  rearrangements.<sup>3</sup> Conjugated dienes, in which

(1) Photochemistry of Tricyclo[4.4.1.1<sup>2,5</sup>]dodeca-3,7,9-trienes. II. Part I: K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, **93**, 6693 (1971).

(2) (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 135 (1966).

(3) For recent discussions, see: (a) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957, 3963 (1971); (b) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *ibid.*, **93**, 4304 (1971).

(3) Under the reaction conditions of eq 2 ( $20^\circ$ , 200 atm),  $H_2$  does not react with the polymerization product  $[(C_5H_5)_2Mo]_2$ .

(4) J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2045 (1971).

(5) R. H. Marvich and H. H. Brintzinger, *ibid.*, **93**, 2046 (1971).

(6) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *ibid.*, **94**, 1219 (1972).

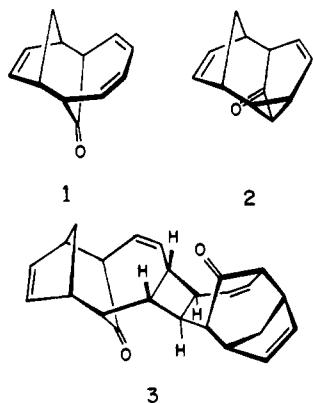
(7) R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1155 (1967).

(8) A solution in toluene- $d_6$  exhibits an nmr spectrum with ten equivalent and ten inequivalent methyl groups which can be interpreted as being due to a sterically hindered dimer.

(9) An increased tendency of the permethyl derivative to form a monomeric species is also observed in the titanocene system. See ref 6.

intersystem crossing is similarly inefficient,<sup>4</sup> undergo isomerization or cyclization upon direct photolysis,<sup>5</sup> and isomerization or dimerization upon sensitized photolysis.<sup>6</sup>

Direct irradiation or triplet-sensitized photolysis of **1** in polar solvents led to the formation of **2** (~60%) as the major product.<sup>7a</sup> Triplet quenchers such as cyclohexadiene, naphthalene, and piperylene had very little effect on the efficiency of formation of **2**.



Irradiation of a  $10^{-2}$  M solution of **1** in cyclohexane resulted in formation of the dimer **3** (~70%) as the major product.<sup>7b</sup> The dimerization was sensitized by triphenylene in cyclohexane and was quenched by oxygen, 0.1 M 1,3-cyclohexadiene, and 0.1 M piperylene, but not by 0.1 M naphthalene, indicating a triplet energy of 55–60 kcal/mol. Direct or sensitized photolysis of **1** in  $10^{-2}$  M solutions in benzene led to the formation of both **2** and **3**.

The structure of **2** (mp 200–205°)<sup>8</sup> was deduced from the ir (KBr; 5.98  $\mu$ ), uv [ $\lambda_{\text{max}}^{\text{EtOH}}$  296 nm ( $\epsilon$  100)], and nmr spectra. A complete analysis of the nmr spectra was accomplished by double resonance experiments in several solvents and with added Eu(fod)<sub>3</sub> shift reagent.

The dimeric nature of **3** [mp 201–202°; ir (KBr) 5.87  $\mu$ ; uv  $\lambda_{\text{max}}^{\text{EtOH}}$  296 nm ( $\epsilon$  25)]<sup>8</sup> could be ascertained from the mass spectrum of octahydro-**3**, formed by catalytic hydrogenation of **3**. The mass spectrum of octahydro-**3** (mp 196–200°) gave a parent ion ( $m/e$  352) as the base peak, while **3** gave only a monomer ion ( $m/e$  172). The nmr spectra of **3** in CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>, and CCl<sub>4</sub> with added Eu(fod)<sub>3</sub> indicated the presence of only 12 types of protons. Assuming head-to-head dimerization—the usual mode of triplet-sensitized diene dimerizations<sup>6</sup>—only the structures of  $C_s$  or  $C_2$  symmetry are possible. Only structure **3** has the proper symmetry and the relative disposition of protons with respect to

(4) W. G. Dauben and W. T. Wipke, "First International Symposium on Organic Photochemistry," Butterworths, London, 1965; J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966.

(5) S. Boue and R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 3226 (1970); J. Satiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970); R. Srinivasan, *ibid.*, **90**, 4498 (1968).

(6) J. Satiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969); J. Satiel, L. Metts, A. Sykes, and M. Wrighton, *ibid.*, **93**, 5302 (1971); W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969).

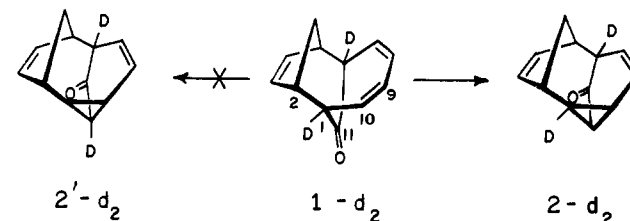
(7) (a) Direct photolyses were carried out in methanol or acetonitrile solutions with light of 254, 300, or 366 nm. Sensitized photolyses were performed in neat acetone or with benzophenone or triphenylene in acetonitrile under conditions where the sensitizer absorbed >95% of the light. (b) Upon prolonged irradiation in 1 M piperylene, a decarbonylation product is formed, as indicated by gas chromatography-mass spectral analysis. Attempted isolation of this thermally labile product has so far failed.

(8) All new compounds gave spectral and elemental analyses in accord with the assigned structures. Analyses of nmr spectra will be reported in the full paper.

the two carbonyl oxygens compatible with the nmr chemical shifts observed upon addition of Eu(fod)<sub>3</sub> to a solution of **3**. Most dramatically, the cyclobutane hydrogens  $\alpha$  to the carbonyl shift to a lesser extent (+1.7 and +1.0 ppm). Thus, dimerization occurs on the less-hindered face of the diene to give the cis-fused cyclobutane of  $C_2$  symmetry.

Cyclopropane **2** could be the product of two different [ $\pi_2\alpha + \sigma_2\alpha$ ] rearrangements, as shown in Scheme I.

Scheme I



The dideuterated adduct **1-d<sub>2</sub>** would produce **2-d<sub>2</sub>** by 10–11 and 1–9 bond formation (an oxa di- $\pi$ -methane rearrangement<sup>3,9</sup>), while **2'-d<sub>2</sub>** would result from 2–10 and 1–9 bonding. Photolysis of **1-d<sub>2</sub>**, prepared from 2,7-dideuteriotropone<sup>10</sup> and cyclopentadiene, gave **2-d<sub>2</sub>** uncontaminated by **2'-d<sub>2</sub>**.

The absorption spectrum of **1** in cyclohexane consists of an  $n-\pi^*$  absorption [ $\lambda$  325 ( $\epsilon$  150), 314 (360), 303 (440), and 292 nm (460)] which borrows intensity<sup>11</sup> from a charge-transfer absorption [ $\lambda \approx 215$  nm ( $\epsilon \approx 5000$ )], and a diene  $\pi-\pi^*$  absorption [ $\lambda$  268 ( $\epsilon$  5400), 259 nm (4600)] which is only slightly different from the absorption spectrum of the alcohol formed by LiAlH<sub>4</sub> reduction of **1**.<sup>2</sup> In the polar solvent ethanol, the  $n-\pi^*$  absorption is broadened, but the onset of absorption is unchanged. The unusual solvent dependence compared to other  $n-\pi^*$  transitions<sup>12</sup> is undoubtedly due to charge transfer (diene  $\psi_2 \rightarrow$  carbonyl  $\pi^*$ ) which results in nearly identical polarity of ground and  $n-\pi^*$  singlet states.<sup>13</sup>

(9) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).

(10) K. N. Houk, Dissertation, Harvard University, 1968; N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, 109 (1971).

(11) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); A. Moscovitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962); J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, pp 165–168.

(12) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 293ff; for recent examples, see G. March, D. R. Kearns, and K. Schaffner, *J. Amer. Chem. Soc.*, **93**, 3129 (1971); W. A. Spitzer and M. S. Kellogg, *ibid.*, **93**, 3674 (1971).

(13) CNDO-Cl calculations using the parameterization of Jaffé and Del Bene<sup>14</sup> indicate the following. There are symmetry-determined ground-state interactions between the diene and carbonyl chromophores, but configuration interaction is of major importance in determining both the position and intensity of the absorptions. The  $n-\pi^*$  absorption in the  $C_2$  conformation is intensified by mixing with a charge-transfer configuration (diene  $\psi_2 \rightarrow$  carbonyl  $\pi^*$ ), resulting in nearly identical polarity of  $n-\pi^*$ ,  $n-\pi^*$ , and ground states. Charge transfer of a different type intensifies the  $n-\pi^*$  transition in the  $C_2$  conformation. In the triplet manifold a third state ("<sup>3</sup>CT," involving charge transfer into the diene and consisting of about 50% of a diene  $\psi_2 \rightarrow$  diene  $\psi_4$  configuration) intervenes between the  $^3n-\pi^*$  and diene  $^3\pi-\pi^*$  states. In the  $C_2$  3,5-cycloheptadienone, <sup>3</sup>CT is nearly degenerate with  $^3n-\pi^*$ , which could lead to rapid intersystem crossing, while in the  $C_2$  conformation, <sup>3</sup>CT lies considerably below  $^3n-\pi^*$  so that intersystem crossing would be expected to be relatively inefficient.<sup>15</sup> In simple  $\beta,\gamma$ -unsaturated ketones, the lowest singlets and lowest triplets consist of different electronic configurations, suggesting that the "spin-correlation" effects observed in those systems are due to differences in orbital occupancy in the lowest singlet and triplet states rather than to differences in spin densities alone.<sup>3b</sup>

The photochemistry of **1** provides an interesting contrast to the photochemistry of monocyclic cycloheptadienones. Direct irradiation of cyclohepta-3,5-dienone (**4**) leads to decarbonylation, while triplet-sensitized photolysis gives the cyclobutene.<sup>16</sup> A dibenzo-3,5-cycloheptadienone also decarbonylates upon direct photolysis.<sup>17</sup> 2,2,7,7-Tetramethylcyclohepta-3,5-dienone (**5**) undergoes a [ $\pi 2_a + \sigma 2_a$ ] rearrangement on either direct or sensitized photolysis.<sup>18</sup>

In polar solvents, the behavior of **1** is similar to that of **5**. Intersystem crossing is more efficient than singlet decarbonylation, and the  $^3n-\pi^*$  state (or the " $^3CT$ " state<sup>13</sup>) is lowest in energy, leading to [ $\pi 2_a + \sigma 2_a$ ] rearrangement. In nonpolar solvents, the behavior of **1** is similar to that of **4**. In the latter, the lowest energy diene  $^3\pi-\pi^*$  state undergoes cyclobutene formation, probably *via* the cis,trans diene,<sup>16</sup> while in the more strained **1**, the twisted  $^3\pi-\pi^*$  state attacks ground-state **1** to form dimer. In solvents of intermediate polarity, both reactive triplet states of **1** are populated.

The inefficiency of intersystem crossing and the  $\pi-\pi^*$  nature of the lowest triplet state of **4**, the efficiency of intersystem crossing and the  $n-\pi^*$  (or CT) nature of the lowest triplet of **5**, and the efficiency of intersystem crossing and closeness of the  $\pi-\pi^*$  and  $n-\pi^*$  (or CT) triplet states of **1** suggest that the relative energies of the various states of 3,5-cycloheptadienones are exceedingly sensitive to both symmetry and substituents. Furthermore, the differences in intersystem crossing efficiency in these closely related systems are most likely related to the energy split between  $^1n-\pi^*$  and  $^3\pi-\pi^*$  states.<sup>15</sup>

Kinetic and emission experiments designed to extract rate constants and state energies as a function of solvent polarity are now in progress.

**Acknowledgment.** We wish to acknowledge the financial support of the Research Corporation and of the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professors R. V. Nauman and J. S. Swenton for their valuable insights and encouragement.

(14) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 563 (1969).

(15) M. A. El-Sayed, *ibid.*, **38**, 2834 (1963); *Accounts Chem. Res.*, **1**, 8 (1968); J. Dym and R. M. Hochstrasser, *J. Chem. Phys.*, **51**, 2458 (1969); for recent examples, see R. J. Hoover and M. Kasha, *J. Amer. Chem. Soc.*, **91**, 6508 (1969); L. Singer, *Tetrahedron Lett.*, 923 (1969); note, however, M. Battey and D. R. Kearns, *Chem. Phys. Lett.*, **2**, 423 (1968). In the case of **1**, spin-orbit coupling by mixing of the  $^1n-\pi^*$  state and the diene  $^3\pi-\pi^*$  state will be small (the  $\pi^*$  values are different), but spin-orbit coupling due to mixing of  $^1n-\pi^*$  and  $^3CT$  states will be large.

(16) D. I. Schuster, B. R. Skolnick, and F.-T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968), and references therein.

(17) K. Mislow and A. J. Gordon, *ibid.*, **85**, 3521 (1963).

(18) L. A. Paquette, R. F. Eizember and O. Cox, *ibid.*, **90**, 5153 (1968).

K. N. Houk,\* D. J. Northington

Department of Chemistry, Louisiana State University  
Baton Rouge, Louisiana 70803

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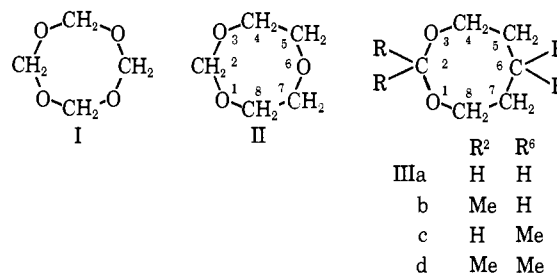
## Conformational Studies of Oxygen-Heterocyclic Eight-Membered Rings

Sir:

The primary reason why cyclooctane and several substituted derivatives, including those having one exocyclic double bond ( $>C=O$  and  $>C=CH_2$ ), prefer

the boat-chair to the diamond-lattice type boat-boat conformation<sup>1</sup> is clearly the transannular repulsion that would exist between two pairs of 1,5-hydrogen atoms in the latter. This repulsion might be reduced if opposing CH groups are replaced by opposing oxygen lone pairs, or even turned into attraction if a CH interacts transannularly with an oxygen lone pair. We have therefore studied the cyclic tetramer of formaldehyde<sup>2</sup> (**I**) as an example of the first situation and cyclic formals of pentane-1,5-diol<sup>3</sup> (**IIIa**) and diethylene glycol<sup>4</sup> (**II**)

Scheme I



as examples of the second situation. Derivatives having *gem*-dimethyl groups in one or two positions (**IIIb-d**), so as to further favor the boat-boat conformation, have also been examined.

The nmr spectrum at 100 MHz of tetrameric formaldehyde (**I**) in  $CDCl_3$  (or  $CH_2Cl_2$ ) is a single line above  $+10^\circ$ , but on cooling it broadens and splits into an AB quartet ( $\Delta\nu_{AB} = 61$  Hz,  $J = 9$  Hz) plus a single line which becomes sharp below  $-40^\circ$ . On further cooling, the relative intensity of the single line decreases rapidly. A plot of  $\ln K$  against  $1/T$  from  $-130$  to  $-40^\circ$  is linear and gives for the equilibrium  $\Delta H = 2.3$  kcal/mol and  $\Delta S = 8.5$  eu, meaning that the "quartet" conformer (or conformational family) preponderant at low temperature has both the lowest enthalpy and the lowest entropy. Extrapolation shows that the "single-line" conformer (or conformational family) must constitute over 60% at room temperature. The infrared spectrum in  $CS_2$  solution also shows two sets of lines whose relative intensity varies with temperature. The same set which gains intensity on cooling becomes more dominant in acetonitrile solution than in  $CCl_4$ , hence belongs to the more polar conformer. This line set also resembles most nearly the spectrum of the crystal, where we assume a symmetrical crown to be present as in the known crystal structure<sup>5</sup> of tetrameric acetaldehyde (all-cis isomer). The correlation of the crystal conformer to the "nmr quartet" conformer is supported by the observation that the strongest Raman line, presumably the ring pulsation mode, is sharp at  $910\text{ cm}^{-1}$  in the solid, but broad at  $925\text{ cm}^{-1}$  with a shoulder at  $910\text{ cm}^{-1}$  in solution. These lines are also seen in the ir spectra. The strongest Raman line of the related but conformationally homogeneous 1,3,5-trioxane is single at  $960\text{ cm}^{-1}$  both in the solid and in solution.<sup>6</sup> The magnitude of the observed dipole

(1) For a review see F. A. L. Anet in "Conformational Analysis," G. Chirudoglu, Ed., Academic Press, New York, N. Y., 1971, p 15.

(2) Y. Miyake, S. Adachi, N. Yamauchi, T. Hayashi, and M. Akimoto, German Patent 1,291,747 (1969).

(3) J. H. Hill and W. H. Carothers, *J. Amer. Chem. Soc.*, **57**, 926 (1935).

(4) P. A. Laurent and P. Tarte, *Bull. Soc. Chim. Fr.*, 718 (1960).

(5) L. Pauling and D. C. Carpenter, *J. Amer. Chem. Soc.*, **58**, 1274 (1936).

(6) A. T. Stair and J. R. Nielsen, *J. Chem. Phys.*, **27**, 402 (1957).