interact more strongly with nucleic acid helices. The construction of these complexes was based on some reasonable assumptions. The credibility of these assumptions is demonstrated by their ability to predict correctly all of the observations thus far recorded. Further testing of these ideas using other types of optically active diammonium salts are in progress.

Experimental Section

Materials. Calf thymus DNA and polyadenylic and polyuridylic acids were obtained from Calbiochem. Polycytidylic and polyinosinic acids were obtained from Miles Labs. L- and D-diaminopropanes were resolved using the procedure outlined by Dwyer, *et al.*[40,41] The specific rotations, $[\alpha]^{35}$D, of the L- and D-diaminopropane dihydrochloride in 1 *N* HCl were found to be −3.82 and +3.48°, respectively. The reported value of $[\alpha]^{18}$D for the L enantiomer of −3.6° is in agreement.[42] L-Diaminopropionic acid hydrochloride was obtained from Biochemical Research, $[\alpha]$D +25.6°. DL-Diaminopropionic acid was synthesized from 2,3-dibromopropionic acid hydrobromide according to the method of Greenstein and Winitz.[43] Solutions of the salts IV, $N^+H_3CHRCH_2N^+H_3$, were prepared in glass-distilled water and carefully adjusted to pH 6.30 by addition of 0.1 *N* sodium hydroxide. In the case of the L-diaminopropionic acid hydrochloride and DL-diaminopropionic acid hydrobromide an equivalent amount of sodium bromide and sodium chloride was added to each, respectively. The final solution in both cases contained the same amount of chloride and bromide ions.

Acknowledgment. This work was supported by the Rutgers Research Council and by Grants GM-13597 and GM-15308 from the U. S. Public Health Service. I am also grateful to Dr. Norman Boggs, III, Mrs. Barbara Gaffney, Miss Roberta Kleinman, Mr. Robert Glaser, and Mr. Robert R. Shimshak for many valuable discussions. Thanks are also due to Miss Betty Hays who drew Figures 1–5 and to the talented and artistic Miss Kleinman for her helpful advice in the drawing of these figures.

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(40) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

(41) The resolution of the diaminopropanes was done by Mrs. Barbara Gaffney.

(42) S. Schnell and P. Karrer, *Helv. Chim. Acta*, **243**, 2037 (1955).

(43) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1961.

Communications to the Editor

The Conformation of *cis,cis*-Cyclodeca-3,8-diene-1,6-dione

Sir:

The conformation of *cis,cis*-1,6-cyclodecadienes has heretofore been discussed in terms of conformers of types I and II, which we designate here as chair and boat, respectively. Generally, opinion has favored the chair form on the basis that nonbonded interactions in the boat form between ring substituents and between the two olefinic bonds are relieved in the chair form.[1] However, the possibility that the boat form is favored because of a sufficiently attractive transannular interaction between olefinic bonds has also been presented.[2] The answer to the question as to which form is favored is of interest not only for testing current methods of conformational analysis but also for providing a starting point for understanding the dynamic and chemical behavior of the ring system. Thus, the recently observed transannular addition of the elements of methyl hypobromite to the tetracarbethoxy derivative IIIa to give a *cis*-decalin ring system[3] suggests the presence of a boat conformer at some stage of reaction. At the present time, however, there is no direct experimental evidence on the conformational bias of *cis,cis*-1,6-cyclodecadienes on which to base a reasonable interpretation of such phenomena.[4] In this communication we present preliminary results of an X-ray crystallographic examination of a derivative of this ring system, diketone IIIb,[1a] which establish, at least for this derivative in the crystalline state, the previously anticipated preference for the chair form.

Crystals of *cis,cis*-cyclodeca-3,8-diene-1,6-dione (IIIb) from chloroform are orthorhombic, with $a = 8.36$, $b = 7.44$, $c = 13.94$ Å. The systematic absences are (hkl) when $k + l = 2n + 1$, $(0kl)$ when $k = 2n + 1$, and $(h0l)$ when $h = 2n + 1$. The space group is therefore either $C_{2v}{}^{17}$-Aba or $D_{2h}{}^{18}$-Abam, and the number of molecules in the unit cell must be a multiple of four. With four molecules per cell, the calculated density is 1.26 g cm^{-3}; larger multiples of this are highly unlikely. Four molecules per cell in space group Aba require a minimum molecular symmetry of C_2-2, and in Abam of C_{2h}-2/m. If the conformation is IIb the molecular twofold axis must be perpendicular to the long axis of the molecule; this twofold axis, in either space group, must be parallel to *c*. Examination of molecular models quickly shows that it is impossible to accommodate the molecules in the unit cell in this way, regardless of how they are rotated about their twofold axes relative to *a* and *b*. If, on the other hand, the conformation is Ib, the molecular twofold axis must

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(1) (a) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960); (b) *ibid.*, 47, 558 (1964); (c) C. Moussebois and J. Dale, *J. Chem. Soc., C*, 264 (1966).

(2) R. M. Gipson, Ph.D. Thesis, University of Texas, 1965.

(3) R. M. Gipson, H. W. Guin, S. H. Simonsen, C. G. Skinner, and W. Shive, *J. Am. Chem. Soc.*, **88**, 5366 (1966).

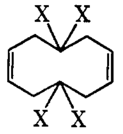
(4) Although equilibration studies have shown that *cis,cis*-1,6-cyclodecadiene is markedly more thermodynamically stable than other cyclodecadiene isomers,[1c,5] the results do not permit an experimental distinction between conformational isomers.

(5) (a) A. J. Hubert, *J. Chem. Soc., C*, 2149 (1967); (b) A. J. Hubert and J. Dale, *ibid.*, 188 (1968); (c) for a review, see J. Dale, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1000 (1966).

coincide with the long axis of the molecule, which, again, must be parallel with *c*, in either space group. The unit cell dimensions are such that this arrangement *is* possible in both space groups. The conformation is accordingly chair form Ib. Space group Abam appears more probable, with a molecular symmetry of C_{2h}-2/m. This work belongs in a rather rarely encountered group of X-ray crystallographic studies in which useful information is obtained merely on the basis of the determination of the space group and unit cell. We do, nevertheless, intend to carry out a complete structure refinement in order to obtain the details of the distribution of the strain in the molecule.

I
chair

II
boat



III
a, X = $CO_2C_2H_5$
b, X,X = =O

The results of this study are in accord with the previously predicted preference of *cis,cis*-1,6-cyclodecadienes for the chair conformation. Moreover, a study of other derivatives of the ring system in solution by nuclear magnetic resonance spectroscopy independently points toward a consistent predilection for this form.[6]

Acknowledgment. We wish to thank the National Science Foundation and the Advanced Research Projects Agency for support of this research.

(6) B. W. Roberts, J. J. Vollmer, and K. L. Servis, *J. Am. Chem. Soc.*, **90**, 5264 (1968).

(7) National Science Foundation Cooperative Fellow, 1965–1967; Stauffer Fellow, 1967–1968.

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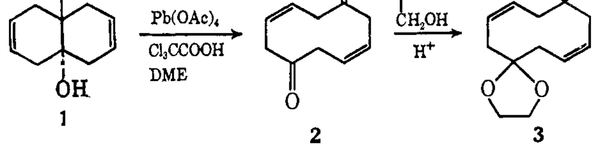
Conformational Mobility in *cis,cis*-1,6-Cyclodecadienes

Sir:

In the past decade nuclear magnetic resonance spectroscopy has proved to be an invaluable tool in gleaning otherwise difficultly accessible information on the structural and chemical dynamic properties of cycloalkanes. The majority of such studies has been confined to the C_6 to C_8 ring systems which, as a consequence, are now relatively well understood.[1] With the exception of the elegant work by Binsch and Roberts on *trans*-cyclodecene,[2] the C_{10} ring system has been largely neglected. In the present investigation we have studied the conformational characteristics of *cis,cis*-1,6-cyclodecadienes, all bearing substituents at positions four and nine.

In a modification of the procedure of Grob and Schiess[3a] *trans*-diol **1** was cleaved with lead tetraacetate in 1,2-dimethoxyethane (DME) to diketone **2**[3] in 60% yield. The latter was in turn converted by acid-catalyzed ketalization with ethylene glycol to diketal **3**[4] in 91% yield. The 100-Mc nmr spectrum of the diketone in $CHCl_3$–$CDCl_3$ at ambient temperature (Figure 1) consists of two symmetrical multiplets centered at 5.65 and 3.21 ppm, respectively (relative areas 1.0:2.0). The spectrum is best described as resulting from an $X_2AA'X_2'$ system[5] and has been analyzed as such to give the following coupling constants:[6] $J_{XX} = J_{X'X'} = -12.0$ cps, $J_{AX} = J_{A'X'} = 8.4$ cps, $J_{A'X} = J_{AX'} = -1.3$ cps, $J_{AA'} = 10.5$ cps, and $J_{XX'} = 0$. Either multiplet when spin decoupled from the other collapses to a sharp singlet. Interpretation of the spectrum as an $X_2AA'X_2'$ system and the results of the spin decoupling of the allylic multiplet imply the equivalence of the allylic protons at ambient temperature. As the temperature of the sample in $CHClF_2$ is progressively lowered, the undecoupled allylic resonance begins to broaden and separates into two distinct multiplets (apparent maximum chemical shift difference = 0.89 ppm) below −100°. The most reasonable explanation for these observations is an interconversion of conformers which, relative to the nmr time scale, is rapid at room temperature but slow at lower temperatures.

The 100-Mc nmr spectrum of diketal **3** in $CHCl_3$–$CDCl_3$ (Figure 2) at ambient temperature is strikingly different from that of diketone **2**. In addition to a sharp singlet at 3.98 ppm for the $-OCH_2CH_2O-$ protons (relative area 8.0) the spectrum consists of symmetrical multiplets at 5.60 and 2.62 ppm and a broad doublet at 1.96 ppm (relative areas 3.9:4.0:4.2) and can be characterized as arising from an ABXX'B'A' spin system. Upon irradiating the multiplet at 5.60 ppm the allylic resonances at 2.62 and 1.96 ppm simplify to an AB system centered at 2.22 ppm ($J_{AB} = -12.9$ cps, $\Delta\nu_{AB} = 0.67$ ppm). Increasing the sample temperature (tetrachloroethylene solvent) leads to a broadening of the resonances of the AB system at 70°, to coalescence at



(1) For some recent examples see: (a) F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965); (b) J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965); (c) J. D. Roberts, *Chem. Brit.*, 529 (1966); (d) M. St. Jacques, M. A. Brown, and F. A. L. Anet, *Tetrahedron Letters*, 5947 (1966).

(2) G. Binsch and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5157 (1965).

(3) (a) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960); (b) K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, 3121 (1967).

(4) The spectroscopic properties and compositional analysis of this compound (mp 185.5–186.0°) were in agreement with the assigned structure.

(5) (a) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); (b) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).

(6) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962) (J_{XX} assumed to be negative).