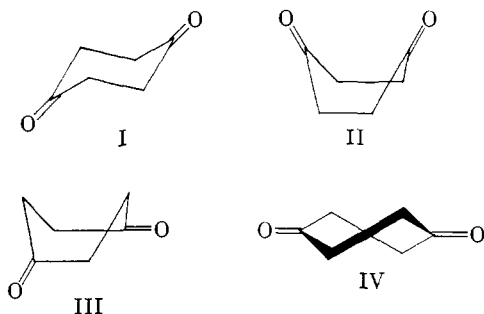


COMMUNICATIONS TO THE EDITOR

CONFORMATIONAL ANALYSIS. XXV. THE MOLECULAR STRUCTURE OF 1,4-CYCLOHEXANEDIONE^{1,2}

Sir:

Dipole moment and Kerr constant measurements on 1,4-cyclohexanedione have been interpreted in terms of an equilibrium between the chair form I and boat forms II and III.^{3,4} It was predicted earlier⁵ from the rotational barriers involved



that the flexible form in fact oscillated between III and an identical form (with carbons 2 and 5 interchanged with 3 and 6) *via* IV. (This oscillation may be referred to as "rocking the boat.") Since in II there are two eclipsed ethanes plus a 1,4 π - π repulsion, this structure should contribute little to molecular properties.

To properly interpret the available data, it was first necessary to determine what the dipole moments of the chair and flexible forms would be. The moment of the flexible form depends on the potential function of pseudo rotation, an approximation of which was deduced by constructing a Dreiding model and measuring for various arrangements both the angle between the dipoles (θ), and the dihedral angles of the ethane units. Assuming ethane type barriers for these units with $V_0 = 2.75$ kcal./mole, the variation in torsional energy with θ was obtained graphically. To this energy was added the van der Waals repulsion between the two carbonyl carbons.⁶ These data yielded in graphic form a function relating θ to the pseudo rotational energy (E_θ) of the flexible form. The rotational barrier of the methylene-carbonyl unit was neglected.

The observed moment of such a flexible system is given by the expression

$$m^2 = \int_{180^\circ}^{86^\circ} \mu^2 \theta e^{-E_\theta/RT} d\theta / \int_{180^\circ}^{86^\circ} e^{-E_\theta/RT} d\theta$$

where μ_θ is the resultant moment corresponding to θ , and is given by $\mu_\theta^2 = 2\mu^2_{CO} (1 + \cos \theta)$, where μ_{CO} is the moment of a single carbonyl group.

(1) Paper XXIV, N. L. Allinger, M. A. DaRooge and C. L. Neumann, *J. Org. Chem.*, in press (1962).

(2) Supported by a grant from the National Science Foundation.

(3) M. T. Rogers and J. M. Cannon, *J. Phys. Chem.*, **65**, 1417 (1961).

(4) C. G. LeFevre and R. J. W. LeFevre, *Rev. Pure Applied Chem.*, **5**, 261 (1955).

(5) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(6) N. L. Allinger, M. A. DaRooge and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961).

The calculation of m was carried out *via* graphic integration for $T = 291^\circ$ and $T = 490^\circ$ K. and gave values of 1.32 and 1.66 D , respectively. These numbers depend on uncertain quantities such as the exact shape of the torsional barrier and are subject to error on the order of a few tenths of a debye. The temperature variation is much less sensitive to such uncertainties, and the predicted increase in moment over the temperature range considered is $0.3 \pm 0.1D$.

The moment of the chair form is zero, but a small "anomalous atomic polarization" of perhaps 10 cc. is expected.⁷ Since the reported moment of the compound⁴ is quite similar to that calculated for the flexible form, it would appear that the latter is in fact the predominant form, contrary to the earlier interpretations.

The difference in enthalpy between the chair and IV is about twice the rotational barrier of a methylene-carbonyl unit. This difference probably is no more than 2 kcal., but its exact magnitude and direction are uncertain.⁵ The entropy of the boat form is expected to exceed that of the chair by an appreciable amount.⁸

The position of the boat \rightleftharpoons chair equilibrium as a function of temperature now can be considered. It is not known which form has the lower enthalpy, but at very high temperatures the greater entropy of the boat form should cause it to predominate. Our interpretation of the reported dipole moment of the compound is that the flexible form strongly predominates at and above room temperature, and there are three checks that have been made on this conclusion. First, since the compound is mainly in the boat form, raising the temperature will cause little change in the boat \rightleftharpoons chair equilibrium, and hence only a very small increase in the dipole moment, which results from an increase of the moment of the flexible form itself. The higher temperature should therefore give a decrease in the orientation polarization. Second, the infrared spectrum of the liquid should show little change with temperature and, further, if the flexible form is the stable one in the crystal also, no bands will appear in the infrared spectrum of the liquid which were not in that of the solid. And third, I has a center of symmetry while the flexible form does not. Coincidences between the Raman and infrared spectra, forbidden for I, therefore are expected.

The orientation polarization was determined over the range 291-324° K. in benzene solution, and appeared to decrease slightly, while the dipole moment appeared to increase very slightly.

Literature³ measurements show a continuing drop in $P_{2\infty}$ with increasing temperature, while μ has continued to increase. This increase relative to the benzene values may be due in part to solvation, while the decrease in $P_{2\infty}$ must result from temperature differences.

(7) E. Charney, *J. Am. Chem. Soc.*, **83**, 578 (1961).

(8) N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

TABLE I
VARIATION OF TOTAL POLARIZATION ($P_{2\infty}$) AND DIPOLE
MOMENT (μ) WITH TEMPERATURE^a

T, °K.	$P_{2\infty}$	μ (D)
291.16	60.8	1.26
298.16	61.4	1.28
311.14	61.7	1.32
323.76	59.7	1.31
468.2	52.8	1.39 ^b
490.3	53.6	1.44 ^b

^a The experimental error is about 1 cc. in $P_{2\infty}$, or 0.02 D. Atomic polarization is neglected throughout. ^b These measurements were made by Rogers and Cannon (ref. 3).

The infrared spectra of the solid and molten dione were determined from 2–15 μ . No bands appeared from the liquid which were not shown by the solid, although the relative areas of certain bands changed slightly upon melting.

The Raman spectrum of the solid compound consisted of seven bands between 726 and 1500 cm^{-1} . There were 24 infrared bands (Nujol mull) in this region, and there was a coincidence for each Raman band. Such a high degree of coincidence is inconsistent with I.

The conclusion drawn is that 1,4-cyclohexanedione exists predominantly in the flexible form near room temperature under all conditions studied in the present work (solid, liquid and solution in inert solvents), and also in the gas phase at higher temperatures. This is the first reported example of a molecule which exists preferentially in the boat form, not because of steric constraints imposed by substituents,⁹ but because of the nature of the ring itself.

Acknowledgments.—The authors are indebted to Professor R. C. Taylor, University of Michigan, for determining the Raman spectrum, and for helpful conversation regarding it, and also wish to thank Professor M. T. Rogers, Michigan State University, for a copy of his manuscript prior to publication.

(9) R. D. Stolow and C. B. Boyce, *J. Am. Chem. Soc.*, **83**, 3722 (1961); and references therein.

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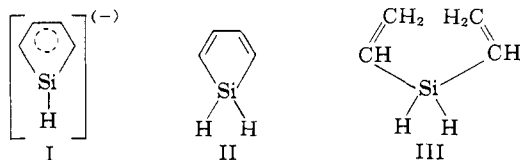
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RECEIVED SEPTEMBER 29, 1961

THE FIRST EXAMPLE OF AN AROMATIC SILICON SYSTEM

Sir:

We wish to report the synthesis and characterization of the anion of silacyclopentadiene (I). This constitutes the first example of an aromatic system containing the silicon atom.



Reduction of 1,1-dichlorosilacyclopentadiene¹ with lithium aluminum hydride in dimethylcarbitol,

(1) R. A. Benkeser, R. F. Grossman and G. M. Stanton, *J. Am. Chem. Soc.*, **83**, 3716 (1961).

resulted in a 60% yield of silacyclopentadiene (II); b.p. 60–62°; n_D^{25} 1.4265; $\lambda_{\text{max}}^{\text{ether}}$ 232 μ ; $\log \epsilon_{\text{max}}$ 3.8.

Anal. Calcd. for $\text{C}_4\text{H}_6\text{Si}$: C, 58.4; H, 7.35. Found: C, 58.27; H, 7.61.

Compound II formed an adduct with hexachlorocyclopentadiene which melted at 35–36°.

Anal. Calcd. for $\text{C}_9\text{H}_6\text{Cl}_6\text{Si}$: C, 30.45; H, 1.70; Cl, 60.00. Found: C, 30.22; H, 1.84; Cl, 60.31.

Conversion of II to the anion I was accomplished with potassium sand in tetrahydrofuran, a solvent in which the product is soluble and colored. The structure of I is indicated by the n.m.r. spectral data: (1) 1,1-dichlorosilacyclopentadiene with a doublet C-H peak (relative areas 1:1) at 2.48 τ ; (2) silacyclopentadiene (II) with doublet C-H peaks at 2.96 τ and Si-H peak at 4.12 τ (relative areas 1:1:1); (3) anion I in tetrahydrofuran with C-H peaks at 2.70 and 2.90 τ and an Si-H peak at 3.95 τ (relative areas 1:1:0.5). There was a noteworthy absence of extraneous peaks.

Treatment of I with excess bromobenzene (after removal of any remaining potassium metal by amalgamation²) yielded a mixture of 1-phenylsilacyclopentadiene and 1,1-diphenylsilacyclopentadiene.¹ Identification of these two products was achieved unequivocally by hydrogenating them catalytically to 1-phenylsilacyclopentane and 1,1-diphenylsilacyclopentane, respectively. The latter two compounds were identical in every respect (*e.g.*, infrared and retention time by vapor phase chromatography) to authentic samples prepared by standard routes.

The reaction of II with potassium proceeded smoothly in non-polar solvents such as benzene or octane, in which I was essentially insoluble and much less reactive toward bromobenzene.

It is striking that under identical conditions divinylsilane (III), which is the open-chain analog of II, is essentially unaffected by potassium sand in benzene or tetrahydrofuran. This would indicate that substantial resonance stabilization of the anion is a prerequisite for metalation on the silicon atom.

It is of interest that the absorption spectrum of I and that of potassium cyclopentadienide in tetrahydrofuran are very similar, implying similar orbital energies. Indeed an LCAO-MO calculation, including silicon d-orbital participation, suggests considerable resonance stabilization.

The foregoing work clearly implies that the silicon atom might be incorporated successfully into an aromatic six-membered ring (*e.g.*, silabenzene) and/or a seven-membered system (*e.g.*, silatropylium cation). Experiments designed to test these possibilities are presently under way in our laboratory.

The authors are grateful to the National Science Foundation for a research grant which made this work possible.

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RECEIVED NOVEMBER 15, 1961

(2) H. Gilman and co-workers, *ibid.*, **74**, 561 (1952).