

SHORT COMMUNICATIONS

THE MOLECULAR CONFORMATION OF TETRAMETHYLCYCLOBUTANE-1,3-DIONE*

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The above compound has been examined in relation to our earlier remarks¹ concerning cyclohexane-1,4-dione.

Experimental

Dielectric constants, densities, refractive indices, and electric birefringences of solutions containing weight fractions w_2 of tetramethylcyclobutane-1,3-dione (m.p. 114–115°, after two sublimations) in carbon tetrachloride have been measured at 25°, increments from solvent‡ to solutions being as follow:

$10^5 w_2$	$10^4 \Delta \epsilon$	$-10^4 \Delta d$	$-10^4 \Delta n$	$-10^{11} \Delta B$
1562	61	167	10	34
3037	124	328	19	66
4825	184	519	30	113

From these data we have: $\Sigma \Delta \epsilon / \Sigma w_2 = 0.410_7$, $\Sigma \Delta d / \Sigma w_2 = -1.076$, $\Sigma \Delta n / \Sigma w_2 = -0.062_6$, and $\Sigma \Delta B / \Sigma w_2 = -0.226 \times 10^{-7}$, so that $\infty P_2 = 49.2$ c.c., $R_D = 37.6$ c.c. (calculated from Vogel's tables,⁴ 38.1 c.c.), and $\infty (mK_2) = -1.2 \times 10^{-12}$.

Proton magnetic resonance spectra, mentioned below, have been taken on a Varian A60 analytical spectrometer, using deuterochloroform (diluted by carbon disulphide 1:1 v/v, for low temperatures) as solvent, with tetramethylsilane as an internal reference.

Discussion

It is now generally accepted⁵ that the four-membered rings in cyclobutane and its derivatives are puckered. Cyclobutanone, on the other hand, by microwave methods,⁶ seems to be planar, while the conformation of tetramethylcyclobutane-1,3-dione (I) has been in question⁷ ever since the unexpectedly high dielectric polari-

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‡ When $w_2 = 0$, $\epsilon_1 = 2.2270$, $d_1 = 1.5845$, $(n_1)_D = 1.4575$, and $(B_1)_D = 0.070 \times 10^{-7}$. Symbols are defined and methods of calculation described in ref. 2, p. 2459, or ref. 3, p. 283.

¹ Chen, C.-Y., and Le Fèvre, R. J. W., *Aust. J. Chem.*, 1963, **16**, 917.

² Le Fèvre, C. G., and Le Fèvre, R. J. W., Ch. 36 in "Physical Methods of Organic Chemistry." (Ed. A. Weissberger.) 3rd Ed. Vol. 1. (Interscience: New York 1960.)

³ Le Fèvre, C. G., and Le Fèvre, R. J. W., *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

⁴ Vogel, A. I., *J. Chem. Soc.*, 1952, 514.

⁵ Lambert, J. B., and Roberts, J. D., *J. Am. Chem. Soc.*, 1963, **85**, 3710, and references therein.

⁶ Bauder, A., Tank, F., and Günthard, H. H., *Helv. Chim. Acta*, 1963, **46**, 1453.

⁷ Huber, H., and Wright, G. F., *Canad. J. Chem.*, 1964, **42**, 1446, and references therein.

zation of this substance at radio frequencies was first noted,⁸ and despite the evidence for planarity provided by an electron diffraction study by Lipscomb and Schomaker⁹ followed by an X-ray analysis by Friedlander and Robertson.¹⁰

Our measurements, giving a total polarization of 49.2 c.c. and a molar refraction of 37.6 c.c., are in satisfactory agreement with previous work on (I) as a solute¹¹ or as a gas.¹² By ordinary procedures the apparent polarity from these data would be *c.* 0.7 D. In view of remarks by Huber and Wright⁷ such a result might not be wholly due to high atomic polarization; however, dielectric loss determinations by Dicarlo and Smyth¹³ suggest that the "true" moment cannot be greater than 0.1 D. On this question the molar Kerr constant now recorded for (I) should have relevance.

In Figure 1(a) we show the planar form as specified (in the crystal) by Friedlander and Robertson,¹⁰ situated within rectangular axes *X*, *Y*, and *Z*. If puckered forms are generated from 1(a) merely by folding about the *Y* axis they will appear as in 1(b).

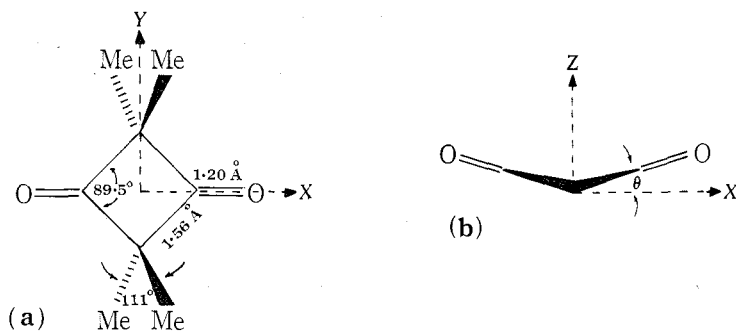


Fig. 1.—Possible forms of tetramethylcyclobutane-1,3-dione. (a) Planar; (b) puckered.

Using the bond polarizabilities* listed in ref.¹⁴ in conjunction with a carbonyl moment of 2.7 D, we calculate the molar Kerr constants and polarities expected for models 1(a) and 1(b) to be as in Table I.

The fact that the observed $\infty(mK_2)$ is algebraically negative implies that (I) is not rigidly planar as a solute. Noting that the mK values in Table I appear approximately predictable from θ° by the equation:

$$10^{12} mK = 3.9 - 0.256\theta^2$$

it follows that for a single species to have an mK of -1.2×10^{-12} requires a θ of

* Quoted here, and throughout, in 10^{-24} c.c. units.

⁸ Angus, W. R., Leckie, A. H., Le Fèvre, C. G., Le Fèvre, R. J. W., and Wassermann, A., *J. Chem. Soc.*, 1935, 1751.

⁹ Lipscomb, W. N., and Schomaker, V., *J. Chem. Phys.*, 1946, **14**, 475.

¹⁰ Friedlander, P. H., and Robertson, J. M., *J. Chem. Soc.*, 1956, 3083.

¹¹ Hammick, D. L., Hampson, G. C., and Jenkins, G. I., *J. Chem. Soc.*, 1938, 1263.

¹² Coop, I. E., and Sutton, L. E., *J. Chem. Soc.*, 1938, 1269.

¹³ Dicarlo, E. N., and Smyth, C. P., *J. Am. Chem. Soc.*, 1962, **84**, 1128.

¹⁴ Le Fèvre, R. J. W., *J. Proc. R. Soc. N.S.W.*, 1961, **95**, 1.

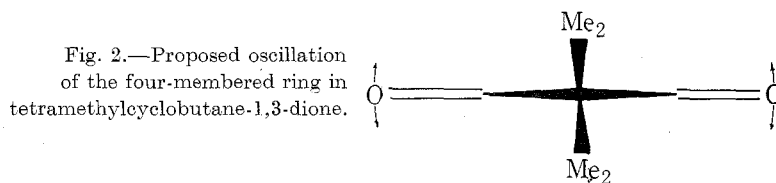
4.46°. However, p.m.r. spectra of (I), recorded at 40° and -60°, show no evidence of non-equivalent protons, displaying at both temperatures only one sharp single peak (τ 8.71 p.p.m. at 40°, 8.64 p.p.m. at -60°).

TABLE I
PRINCIPAL POLARIZABILITIES, DIPOLE MOMENTS, ETC., FOR TETRAMETHYL-
CYCLOBUTANE-1,3-DIONE*

μ_z (D)	θ°	b_x	b_z	$10^{12} mK$ (calc.)
0	0	15.87	12.75	+3.9
0.1	1.0 ₅	15.87	12.75	+3.5
0.2	2.0 ₅	15.86	12.76	+2.6
0.4	4.4	15.85	12.77	-0.9
0.5	5.3	15.84	12.78	-3.5
0.7	7.5	15.79	12.83	-10.3

* $b_y = 14.88$ for all values of θ° .

All the above observations, including the "anomalous" orientation polarization of c. 10 c.c., become understandable if (I) is a flexible structure which oscillates through a mean plane, as suggested in Figure 2. This explanation parallels that



previously given for 1,4-cyclohexanedione¹ except for the detail that the four-membered ring compound is planar in the crystal¹⁰ while the six-membered ring is a slightly irregular version^{15,16} of the conformation shown as (III) by Chen and Le Fèvre.¹

¹⁵ Groth, P., and Hassel, O., *Acta Chem. Scand.*, 1964, **18**, 923.

¹⁶ Mossel, A., and Romers, C., *Acta Crystallogr.*, 1964, **17**, 1217.