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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIKETENE

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The structure of diketene has been the subject of many investigations which include ultraviolet, Raman, infrared, and electron diffraction studies, as well as many chemical ones. Reviews of the problem have been contained in articles by Whiffen and Thompson (1) and Boese (2), to mention only two. Good evidence has also been presented to show that diketene is an equilibrium mixture (3).

In the present investigation we have used the x-ray methods worked out in this laboratory for low temperature problems (4). The space group is $P2_1/c$ with four molecules in a unit cell having dimensions a = 4.00, b = 20.67, c = 5.11 Å and a monoclinic angle of 101.8°.

Trial and error methods eventually proved successful, and electron density maps were made from precession camera data (Mo — K_α radiation) for four different zones. The $hk\bar{h}$ Fourier showed the molecule edge on and established its planarity. Of the remaining three, both the $0kl$ (Fig. 1) and $hk0$ maps showed the molecule without overlap.[1]

Disregarding bond lengths the relative positions of atoms given by the electron density maps could correspond to either 3- or 2-buteno-β-lactone. The bond length calculations, however, show that the molecule, or at least the low-temperature isomer, is 3-buteno-β-lactone. Values found for the bond lengths (±0.06 Å) and angles (±2°) are as follows (see Fig. 2):

BOND NUMBER	LENGTH, Å	ANGLE NUMBER	ARC, °
1	1.35	θ_1	130
2	1.39	θ_2	94
3	1.40	θ_3	136
4	1.24	θ_4	89
5	1.46	θ_5	94½
6	1.48	θ_6	121
		θ_7	145
		θ_8	83

These values should probably be considered about normal, in view of the rather high limits of error, with the exception of the C—C bond marked 5. Some shortening here could be attributed to hyperconjugation. In support of this view is the fact that Θ_6 is appreciably smaller than Θ_7, which would be expected if bond 5 had any significant double bond character. Similar remarks, to a lesser degree, may apply to bond 6.

We wish to thank the Union Carbide and Carbon Company for supplying the sample of diketene used in this study. Financial support (to L. K.) provided

[1] Details of this structure determination will be published in the *Acta Crystallographica*.

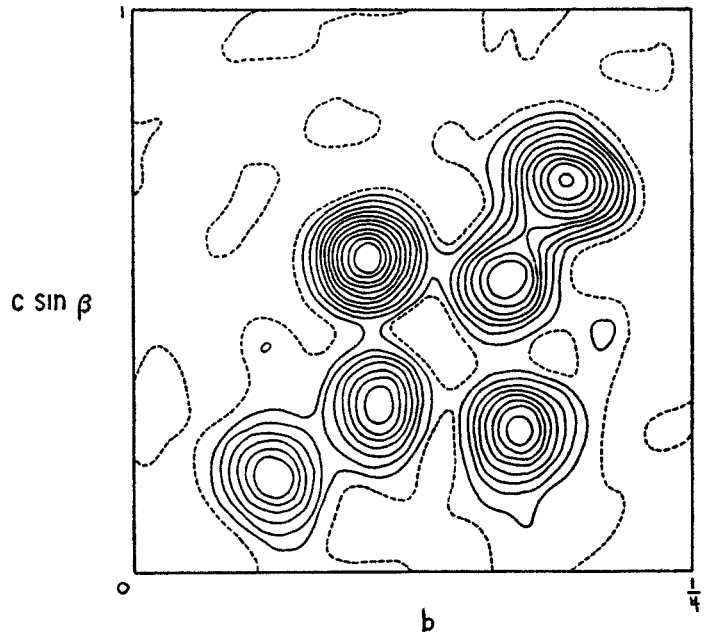

FIGURE 1. PROJECTION OF THE ELECTRON DENSITY ALONG [100]. Contours are approximately in electrons/Å^3, the one electron contour being broken

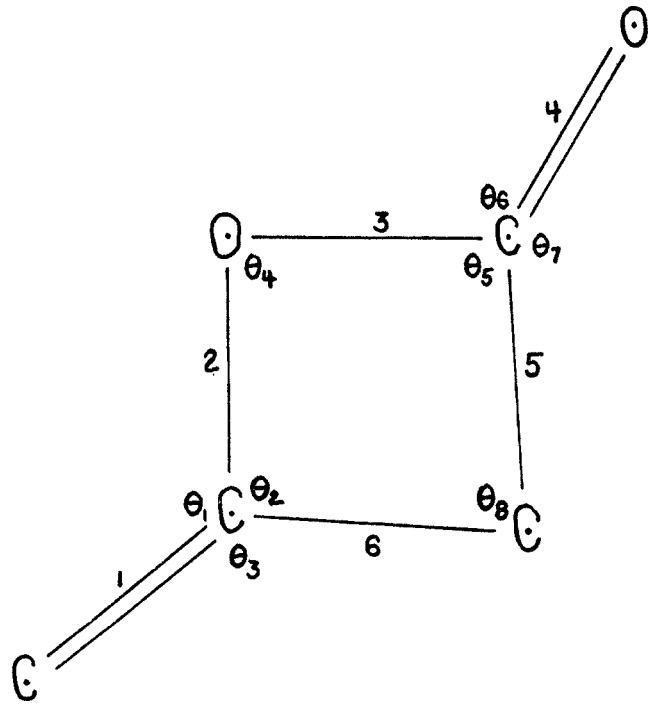

FIGURE 2. THE MOLECULE OF DIKETENE

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