

Fig. 1. Electron density map of asparagine monohydrate, projected on  $y$ - $z$  plane, with molecule superposed.

Steward and Thompson have suggested that the properties of asparagine may be due to the formation of a cyclic structure, with the carboxyl combined in the ring; and they indicate how some aspects of the behavior of this molecule may be accounted for by such a structure. Huggins (3) has suggested an alternative structure in which the carboxyl and amide groups are coiled so that these two groups are in proximity.

At the suggestion of Steward (4), an x-ray structure analysis of asparagine has been carried out, in the hope that information might be derived which would shed light on the differences in behavior between asparagine and glutamine. The cell and symmetry of asparagine were first reported by Bernal (5), but his analysis was not carried to the point where the molecular shape and association could be established.

Single-crystal patterns from the L-asparagine monohydrate  $C_4H_8O_5N_2 \cdot H_2O$  (4) provide the following information: (i)  $a = 5.58 \pm 0.01$  Å,  $b = 9.83 \pm 0.02$  Å, and  $c = 11.81 \pm 0.02$  Å; (ii) space group  $P2_12_12_1$ ; and (iii) 4 molecules per cell. Three-dimensional data have been collected with  $CuK\alpha$  radiation and a Weissenberg camera. Interpretation of a three-dimensional Patterson map, computed on X-RAC (6), provided a successful trial structure. Successive refinement of an electron density projection on (100), using X-RAC and S-FAC alternately, resulted in the electron density contour map shown in Fig. 1. All atoms are clearly resolved, and the  $y$  and  $z$  parameters are sufficiently accurate to permit calculation of a three-dimensional density distribution, which is now being refined.

From the (100) projection of Fig. 1 and packing considerations, the general features of the structure are clear. The succinic acid part of the molecule is

in a trans-configuration. A similar configuration is found by Pasternak, Katz, and Corey (7) in glycyl-L-asparagine. The structure is held together by a three-dimensional network of hydrogen bonds. A water molecule appears nearly at the center of a tetrahedron formed by three oxygen atoms and the nitrogen atom of the  $\alpha$ -amino group.

Even in its present stage, this analysis clearly reveals that the cyclic structure is not present in the crystalline monohydrate. This, of course, does not establish that such a cyclic configuration is impossible in solution.

#### References and Notes

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4. We are grateful to Steward for suggesting the problem and furnishing material for the study; to the Rockefeller Foundation for a fellowship for one of us (O. C.-C.); to the National Institutes of Health, Institute of Arthritis and Metabolic Diseases, for grant A-228 under which much of the research was conducted; and to the Office of Naval Research, contract No. N6onr-26916, T. O. 16, for support of calculations on X-RAC and S-FAC. We also thank P. F. Eiland for much helpful advice.
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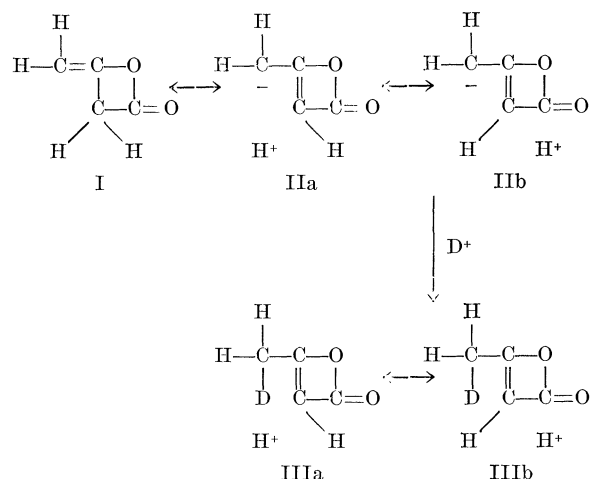
## Hyperconjugation in Ketene Dimer

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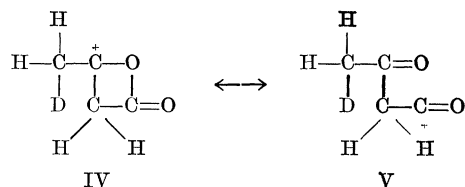
The 3-butenic  $\beta$ -lactone structure (I) for diketene is fairly conclusively established by ozonolysis, which gives formaldehyde and malonic acid (1); by bromination with N-bromosuccinimide, which gives only  $\beta$ -bromoacetoacetic derivatives (2); and by methanolysis with methanol-d, which gives only methyl  $\gamma$ -deuteroacetoacetate (3). Adequate explanations for the reactions of diketene based on the 3-butenic  $\beta$ -lactone structure are necessary to complete the general acceptance of this structure because the acetylketene structural possibility offers such obvious and convenient explanations for most diketene reactions that there is a persistent tendency (3, 4) to use this acetylketene structure in describing diketene reactions. The purpose of this comment is to point out that hyperconjugation possibilities, along with transformations based on accepted analogies and resulting from such possibilities, which are present in the 3-butenic  $\beta$ -lactone structure, provide a simple and previously unnoted explanation for diketene reactions.

Hyperconjugation possibilities in the 3-buten-2-ol structure (I) include contributions from two structures IIa and IIb, either of which permit attack by a positive fragment, such as the proton or deuteron, at the exocyclic methylene carbon atom to give IIIa-IIIb.



These hyperconjugation resonance structures involve no greater charge separation than previously considered resonance structures involving a cyclic oxonium atom. Moreover, since deuterium exchange with the hydrogen atoms involved in the "no bonds" has been shown (5) to be nonexistent, such structures as IIIa-IIIb are entirely consistent with the absence of  $\alpha$ -deuteration during the methanolysis with methanol-d. In fact, only after it is known that there is no exchange of  $\alpha$ -hydrogen atoms with deuterium is it likely that these hyperconjugation structures would be seriously considered.

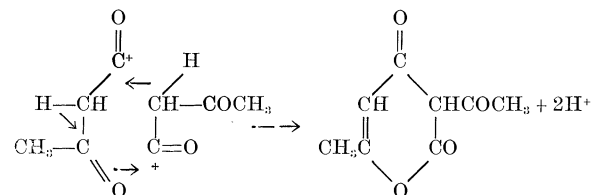
Conversion of IIIa-IIIb to IV represents the normal course of the mechanism of addition reactions in which hyperconjugation is involved. Reactions of IV, such as combination with a methoxide ion, will obviously not give the acetoacetate structures actually obtained. Rearrangement of IV to the acyloxy ion V provides the structural entity that does explain acetoacetate formation. Analogies for the two steps involved in the rearrangement of IV to V are known. The conversion of a carbonium ion (in which the carbonium carbon is linked to an oxygen atom) to a carbonyl group is postulated as one step in the gen-



erally accepted mechanism for the pinacol rearrangement (6), and formation of an acyloxy ion from an ester is postulated as one step in accepted mecha-

nism for Friedel-Crafts acylations and for the sulfuric acid catalyzed hydrolysis of ethyl 2,4,6-trimethylbenzoate (7).

The acyloxy ion V is structurally similar to the acetylenic structure. It can be regarded as the product formed by addition of a proton to acetylenic ketene. The result is that the ease and convenience associated with reaction concepts based on acetylenic ketene are readily transferred to concepts based on this conversion. For example, the formation of dehydroacetic acid from diketene can be formulated as follows:



Acceptance of this hyperconjugation-acyloxy ion concept for the structure and reactions of 3-buten-2-ol  $\beta$ -lactone will permit clarification of much of the confusion in the literature on diketene reactions.

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### Blood Studies of Red Sindhi-Jersey Crosses: III. Effect of a Fixed Hot Environment on Blood Constituent Levels of Jerseys and Sindhi-Jersey Crosses

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One of the principal problems in the general program of developing strains of dairy cattle better adapted to subtropical climates has been to discover some easily measured morphological or physiological characteristic that could be used as an index of the animal's heat tolerance. The object of this study is to present the results of an attempt to correlate certain readily measured blood constituent levels (hemoglobin, hematocrit, plasma calcium, and plasma inorganic phosphorus) with heat tolerance.

Rusoff *et al.* (1) reported that higher hemoglobin, hematocrit, and plasma inorganic phosphorus levels exist in the blood of Sindhi-Jersey daughters than in their Jersey dams. Similarly, Blincoe *et al.* (2) re-