

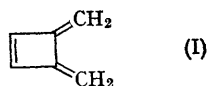
The Rotational Constants and Dipole Moment of 3,4-Dimethylenecyclobutene

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THE classification of conjugated hydrocarbons into alternant and nonalternant systems¹ was proposed when non-neighbour core resonance integrals were not included in π -electron molecular-orbital calculations. Brown and Burden² have pointed out that according to its classical structure 3,4-dimethylenecyclobutene (I) is an alternant hydrocarbon, but, with inclusion of non-neighbour core resonance integrals in the calculation, predicted that it would possess a dipole moment. Thus the existence and size of the dipole moment in 3,4-dimethylenecyclobutene is of considerable significance in an evaluation of the alternant: nonalternant classification.

The microwave spectrum of 3,4-dimethylenecyclobutene has been measured between 8.0 and 26.5 GHz. The spectrum shows only *b*-type



transitions and gives the rotational constants $A = 5569.93$; $B = 4261.79$; $C = 2313.55$ MHz. The inertial defect of 0.0754 a.m.u. \AA^2 indicates that the molecule is planar. Measurements of the Stark effects of four low- J lines gives a dipole moment of 0.618 ± 0.011 D.

The experimental dipole moment is in close agreement with that calculated for 3,4-dimethylenecyclobutene (0.71 D with the ring positive)^{2,3} when non-neighbour core resonance integrals are included and the geometry assumed in the theoretical study is in very good accord with the measured rotational constants (it predicts them within 1%). If a nonzero C-H σ -bond moment is assumed then the resultant σ -electron contribution to the dipole moment cancels.† Thus the observed dipole moment must be ascribed essentially to a non-uniform π -electron distribution as it seems unlikely that C-C σ -bond polarities could make more than a minor contribution to the total moment. This non-uniform π -electron distribution represents a breakdown in the alternant : non-alternant classification.

The calculated dipole moment is sensitive to the value employed for the cross-ring resonance integral and insensitive to other parameters including small changes in skeletal geometry

(*e.g.*, changes in the assumed geometry that preserve compatibility with the observed rotational constants alter the calculated moment by only one or two units in the second decimal). The non-neighbour resonance integrals were estimated by assuming a proportionality to overlap integrals. The agreement between experimental and calculated polarities suggests that this method of estimating non-neighbour resonance integrals gives reliable results.

Accurate geometries for 3,4-dimethylenecyclobutene and fulvene, in addition to the dipole moment of fulvene are at present being determined. It is hoped that results will help define the variation of the π -electron resonance integral with internuclear distance. Work is also in progress to examine more closely the polarity contributions of the σ -electrons in these systems using all-valence-electron SCF-MO methods.

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† When the methylene groups have 120° bond angles and the ring CH directions bisect the external ring angles.

¹ C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 192.

² R. D. Brown and F. R. Burden, *Chem. Comm.*, 1966, 448.

³ R. D. Brown, F. R. Burden, and G. M. Mohay, *Austral. J. Chem.*, in the press; R. D. Brown and B. A. W. Collier, *Theor. Chim. Acta*, 1967, **7**, 259.