

SHORT COMMUNICATIONS

3,4-DIMETHYLENECYCLOBUTENE: AN ISOLABLE ANTIAROMATIC MOLECULE?

By B. A. HESS, JR,* and L. J. SCHAAD*

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(1) The properties of 3,4-dimethylenecyclobutene (1) are unusual for an alternant conjugated hydrocarbon and have caused a great deal of recent interest.¹⁻⁸ Although (1) is an isomer of benzene and might have been expected to exhibit some aromatic stabilization,^{1,8} it does not.^{4,5} The compound has a large dipole moment (0.618 D)⁶ in spite of the fact that in the Hückel approximation all alternant hydrocarbons should have zero moment. The bonds within the ring are of varying length,³ which again indicates lack of aromatic character.

We have recently introduced a new method of obtaining HMO resonance energies of cyclic conjugated hydrocarbons.⁹ The resonance energy of a compound is determined by subtracting from the total HMO π energy the π energy of an additive structure calculated with bond energies obtained from acyclic polyenes. Compounds with a positive resonance energy are found to be aromatic; with no resonance energy, polyolefinic or nonaromatic; and with a negative resonance energy, antiaromatic. An excellent correlation was found for a wide range of benzenoid and nonbenzenoid compounds.⁹⁻¹² The one apparent exception to this correlation was dimethylenecyclobutene which has a resonance energy per π electron (REPE) of -0.028β , but yet is isolable.

Our prediction that (1) should be antiaromatic, that is of lower stability than acyclic polyolefins, did not at first appear to be borne out by experiment. Although (1) does readily polymerize in the presence of air, it is stable for long periods at room temperature when stored under nitrogen.⁵ Its apparent thermal stability is in contrast

* Department of Chemistry, Vanderbilt University, Nashville, Tenn., U.S.A. 37235.

¹ Griffith, D. W. T., Kent, J. E., and O'Dwyer, M. F., *Aust. J. Chem.*, 1972, **25**, 241.

² Coller, B. A. W., Heffernan, M. L., and Jones, A. J., *Aust. J. Chem.*, 1968, **21**, 1807.

³ Skancke, A., *Acta chem. scand.*, 1968, **22**, 3239.

⁴ Allinger, N. L., Gilardeau, C., and Chow, L. W., *Tetrahedron*, 1968, **24**, 2401.

⁵ Huntsman, W. D., and Wristers, H. J., *J. Am. chem. Soc.*, 1967, **89**, 342.

⁶ Brown, R. D., Burden, F. R., Jones, A. J., and Kent, J. E., *Chem. Commun.*, 1967, 808.

⁷ Brown, R. D., and Burden, F. R., *Chem. Commun.*, 1966, 448.

⁸ Blomquist, A. T., and Maitlis, P. M., *Proc. chem. Soc.*, 1961, 332.

⁹ Hess, B. A., Jr, and Schaad, L. J., *J. Am. chem. Soc.*, 1971, **93**, 305.

¹⁰ Hess, B. A., Jr, and Schaad, L. J., *J. Am. chem. Soc.*, 1971, **93**, 2413.

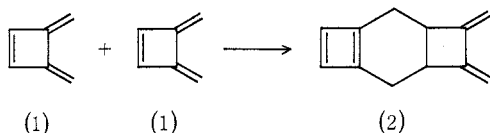
¹¹ Hess, B. A., Jr, and Schaad, L. J., *J. org. Chem.*, 1971, **36**, 3418.

¹² Schaad, L. J., and Hess, B. A., Jr, *J. Am. chem. Soc.*, 1972, **94**, 3068.

to the low stability of other compounds which we have calculated to be antiaromatic. For example, benzocyclobutadiene ($\text{REPE} = -0.027\beta$) cannot be isolated but is obtained as a dimer which may arise by way of a self-Diels-Alder reaction.¹³

However, whether or not a compound can be isolated must depend not on its stability alone, but also on the stability of possible conversion products. A compound predicted to be stable may not be isolable because it can go to products still more stable. Conversely, a high-energy compound may be isolable because it has no easy conversion routes available.

Consideration of potential reaction pathways of (1) in the absence of air or free radical sources shows it to belong to the second class. It would appear that the only energetically feasible reactions of (1) at room temperature are cycloadditions. But *all* potential cycloadditions with the exception of [2+2] cycloadditions, which have been shown to be thermally forbidden reactions,¹⁴ would yield cyclobutadiene derivatives. An example is:



We therefore suggest that (1) may be a stable antiaromatic molecule. Note that the predicted antiaromaticity is due entirely to destabilization by cyclic conjugation. The calculations do not include the large additional destabilization caused by strain in the four-membered ring.

No conclusions about the energetics of the dimerization of (1) to give (2) or other cyclobutadiene derivatives can be made directly by comparison of REPE values. Rather, the total energies must be considered. Although one might attempt to make a conclusion based on the total π energies alone, we feel that the change in the σ structure makes any such conclusion rather tenuous. However, it has been shown that tetracyanoethylene does not react with (1) in a Diels-Alder fashion.² On the basis of this and the well known instability of cyclobutadiene derivatives, we suggest that the dimerization above is unlikely to occur.

3,4-Dimethylenecyclobutene appears to be unique as we have so far found no other example of a planar conjugated cyclic hydrocarbon which is antiaromatic and isolable. Benzene, fulvene, and dimethylenecyclobutene thus form an interesting set of isomers, being respectively aromatic, nonaromatic, and antiaromatic.

¹³ Cava, M. P., and Napier, D. R., *J. Am. chem. Soc.*, 1957, **79**, 1701.

¹⁴ Woodward, R. B., and Hoffmann, R., *Angew. Chem. int. Edn*, 1969, **8**, 781.