CUMULENE CARBENES IN SPACE AND IN THE LABORATORY

J. M. VRTILEK, C. A. GOTTLIEB, T. C. KILLIAN, and P. THADDEUS
Division of Applied Sciences
Harvard University
Cambridge, MA 02138, U.S.A.

J. CERNICHARO, M. GUÉLIN, and G. PAUBERT
IRAM
Domaine Universitaire de Grenoble
F-38406 St. Martin D'Hères, France

ABSTRACT. Astronomical searches for H_2CCC and H_2CCCC, based on frequencies from our laboratory identifications, have resulted in detections toward TMC–1 and IRC+10216. These new interstellar species are possibly the first of a new family of highly polar carbon chains; they are only the second and third carbenes (carbon molecules with two nonbonded electrons) known in space.

1. Introduction

As part of a long-term investigation of rotational spectra of transient and reactive molecules of astrophysical importance, we recently undertook a laboratory search for several members of a family of highly polar hydrocarbons with linear double-bonded carbon backbones and terminal nonbonded carbene electrons. Two of these, H_2CCC and H_2CCCC, have now been successfully observed in the same cooled acetylene discharge that has been a source of numerous other reactive hydrocarbons (Vrtilek *et al.* 1990; Killian *et al.* 1990). They are remarkable for several reasons: both are isomers of interstellar species, H_2CCC of cyclic-C_3H_2 and H_2CCCC of diacetylene (almost certainly abundant though not directly detected); both are highly polar, with the two nonbonded electrons characteristic of carbenes; and, like a number of other transient interstellar species, both are unsaturated carbon chains.

With highly accurate (~1 km s^{-1} or better in equivalent velocity) frequency predictions in hand, we initiated successful astronomical searches for H_2CCC and H_2CCCC, using principally the IRAM 30 m telescope but also data from the Effelsberg 100 m and the NRAO 43 m (Cernicharo *et al.* 1991*a,b*). Observations were also obtained at Nobeyama (Kawaguchi *et al.* 1991).

Although the smallest H_2C_n molecule, vinylidene, H_2CC, has proven elusive, larger members of this sequence, predicted to be stable and even more polar, are excellent candidates for laboratory and radioastronomical detection, and searches for them are now underway.

2. Rotational Spectra of H_2CCC and H_2CCCC

H_2CCC and H_2CCCC are calculated (DeFrees and McLean 1986; Dykstra, Parsons, and Oates 1979) to be the isomers next in energy above their ground configurations. Very nearly prolate symmetric top molecules, with rotational spectra characterized by strong, harmonically related *R*-

P. D. Singh (ed.), Astrochemistry of Cosmic Phenomena, 23–24.

https://doi.org/10.1017/S0074180900089634 Published online by Cambridge University Press

branch lines, both species have many lines well situated for observation with mm-wave and cm-wave radio telescopes.

Our prediction of a very specific nearly harmonic sequence of doublets in the millimeter-wave rotational spectra of H_2CCC and H_2CCCC was the basis for a systematic laboratory search for these species. In ladders with $K_a > 0$ the slight deviation from symmetry splits energy levels degenerate in the symmetric top case (*K*-doubling). For intermediate values of K_a, here $K_a = 3$, the doublet splitting takes on a distinctive and convenient signature of a few MHz.

Support for our identifications comes from a number of chemical and physical assays, in addition to agreement of the observed spectrum with that expected for molecules with C_{2v} symmetry and the geometry of H_2CCC and H_2CCCC. For H_2CCC we now have conclusive evidence: a full substitution structure (Killian *et al.* 1991, in prep.).

3. Measurements in Space

Our initial identification of H_2CCC in TMC–1 rested on three lines found at the expected frequencies (Cernicharo *et al.* 1991*a*), from which we derived a rotational temperature of 4–6 K, consistent with expectations from other molecules, and a column density of $(2.5 \pm 0.5) \times 10^{12}$ cm^{-2}, smaller by a factor of ~70 than that of the lowest energy isomer, cyclic-C_3H_2. Three lines detected toward IRC+10216 imply a rotational temperature of 25 K and a column density of $\sim 2.6 \times 10^{12}$ cm^{-2}.

Eight mm-wave transitions of H_2CCCC have been assigned toward IRC+10216; all are fit by a single rotational temperature, 20 ± 3 K; the implied column density is $(1.6 \pm 0.4) \times 10^{13}$ cm^{-2}, 6 times that of H_2CCC toward IRC+10216 (Cernicharo *et al.* 1991*b*). Several lines of H_2CCCC have now been found in TMC–1, as for H_2CCC at precisely the expected frequencies (Kawaguchi *et al.* 1991). The column density of H_2CCCC in TMC–1, $\sim 8 \times 10^{12}$ cm^{-2}, is greater, as in IRC+10216, than that of the smaller molecule H_2CCC.

The presence of three closely spaced, low-lying lines, two *ortho* ($2_{12} - 1_{11}$ at 17.79 GHz and $2_{11} - 1_{10}$ at 17.94 GHz) and one *para* ($2_{02} - 1_{01}$ at 17.86 GHz), in the spectrum of H_2CCCC at frequencies conveniently located for radio astronomy permits accurate measurement of the *ortho-para* ratio, hence a possible constraint on proton density, and a search in the two *ortho* lines for the Townes-Cheung effect found in H_2CO.

4. References

Cernicharo, J., Gottlieb, C. A., Guélin, M., Killian, T. C., Paubert, G., Thaddeus, P., and Vrtilek, J. M. 1991*a*, *Ap. J. Letters*, **368**, L39 .

Cernicharo, J., Gottlieb, C. A., Guélin, M., Killian, T. C., Thaddeus, P., and Vrtilek, J. M. 1991*b*, *Ap. J. Letters*, **368**, L43.

DeFrees, D. J., and McLean, A. D. 1986, *Ap. J. Letters*, **308**, L31.

Dykstra, C. E., Parsons, C. A., and Oates, C. L. 1979, *J. Am. Chem. Soc.*, **101**, 1962.

Kawaguchi, K., Kaifu, N., Ohishi, M., Ishikawa, S., Hirahara, Y., Yamamoto, S., Saito, S., Takano, S., Murakami, A., Vrtilek, J. M., Gottlieb, C. A., Thaddeus, P., and Irvine, W. M., 1991, *Pub. A. S. J.*, in press.

Killian, T. C., Vrtilek, J. M., Gottlieb, C. A., Gottlieb, E. W., and Thaddeus, P. 1990, *Ap. J. Letters*, **365**, L89.

Vrtilek, J. M., Gottlieb, C. A., Gottlieb, E. W., Killian, T. C., and Thaddeus, P. 1990, *Ap. J. Letters*, **364**, L53.