for thermal motion, and their standard deviations.

A schematic drawing showing a projection of the structure along the *c* axis is given in Fig. 1.

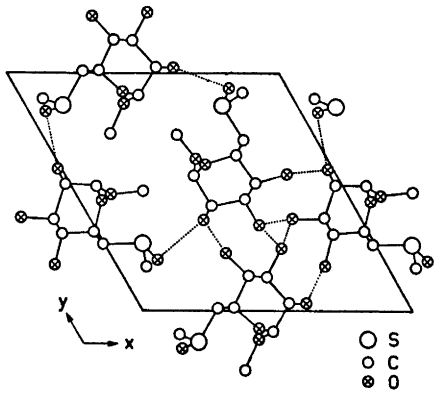

Fig. 1. The structure of methyl-6-deoxy-6-methylsulfinyl-α-D-glucopyranoside. Schematic drawing showing the *xy* projection. Dashed lnes indicate probable system of hydrogen bonds.

Full details of this structure investigation and a discussion of the results will be given elsewhere.

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The crystals were kindly supplied by Dr. Hans Lundström, Institute of Organic Chemistry at this University.

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The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach

V. Tricyclo[1.1.0.0^{2,4}]butane (Tetrahedrane)

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Tricyclo[1.1.0.0 ^{2,4}]butane (tetrahedrane) (Fig. 1) is considered to form the most strained system of the hydrocarbons built up from three-membered rings. One would also expect this, since the angular geometry of tetrahedrane is completely determined by the high symmetry and there are no angular degrees of freedom available for a minimizing of the energy. By contrast, bicyclo[1.0.1]-butane, for instance, has several angular parameters available for this purpose. The bridgehead C–C–H bond is here by Haller and Srinivasan [1] estimated to have a classical valence angle

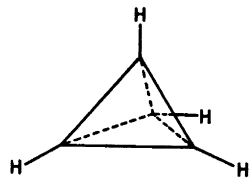

Fig. 1. The valence skeleton of tricyclobutane (tetrahedrane).

of 163° as compared to 144°44′ for the C–C–H bond in tetrahedrane, a value fixed by symmetry. The angle between the triangular planes in bicyclobutane is estimated to be 126° as compared to the symmetry-fixed value of 70°32′ in tetrahedrane. We have also the possibility of varying the conformation of the methylene groups in bicyclobutane, but this is probably of minor importance in this context.

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To this can be added that the C–C interatomic distance seems to vary very little with strain in single bonds.

Tetrahedrane itself is, as yet, merely a hypothetical compound. A derivative, methyltricyclobutanetricarboxylic acid, was reported synthetized by Thorpe and Beesley as early as 1920.[2] However, Larson and Woodward [3] say that numerous attempts to reproduce the synthesis by Thorpe and Beesley have not been succesful but lead to other products. First in 1965 a tetrahedrane derivative seems to have been reported by Masamune and Kato,[4] who prepared diphenyltetrahedrane in low yield by UV irradiation of (Δ^2-2,3-diphenylcyclopropenyl)-acetaldehyde in the form of its tosylhydrazone in tetrahydrofurane in the presence of sodium methoxide.

In these notes we will comment on the strain of tetrahedrane by looking at its valence charge distribution which in a simple way gives a picture of the bonding conditions. The contour maps of the valence electron density of the tetrahedrane molecule in the sections shown here have been obtained by a procedure described earlier.[5] We have only to add that the "molecular value" 1.2 has been used for the exponent of the Slater 1*s* orbitals of hydrogen in both calculation steps (eigenvectors and the density itself).[6] Atomic units are used and the topological levels are 0.01, 0.03, 0.06, 0.09, ... a.u. The geometry used is 1.534 Å for the C–C interatomic distance, and 1.093 Å for the C–H distance as proposed by Baird and Dewar.[9]

Figs. 2, 3, and 4 display topologically the valence charge of tetrahedrane in three pertinent sections of the molecule.

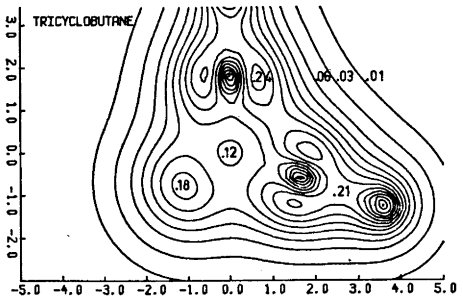

Fig. 2. The valence charge distribution of tricyclobutane in the symmetry plane of the molecule.

From the distribution in the symmetry of the molecule and the surface plane of the tetrahedron formed by the carbon atoms (Figs. 2 and 3) we see that we have two charge maxima outside the inter-

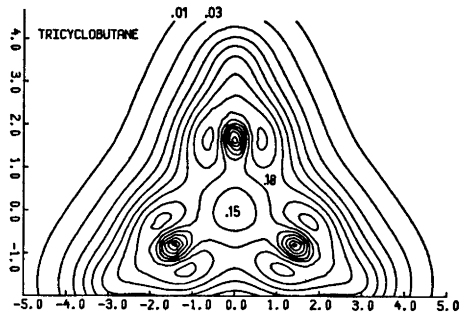

Fig. 3. The valence charge distribution of tricyclobutane in the surface plane of the tetrahedron.

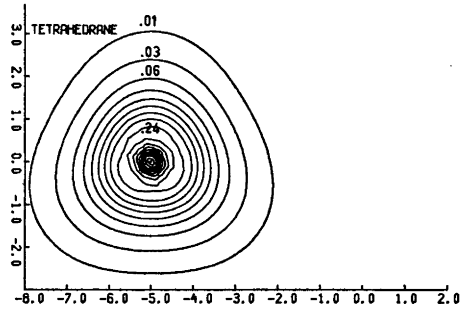

Fig. 4. The valence charge distribution of tricyclobutane in a section through a carbon atom and parallel to the opposite surface of the tetrahedron.

atomic C–C vector (the classical valence line) very similar to those of the C–C bond in cyclopropane.[5] The other maximum on the opposite side of the carbon atom is centered between the two remaining C–C interatomic vectors. Since the symmetry at the carbon atoms is threefold, we have three such pairs of maxima. This heaping up of valence charge can be seen from Fig. 4, which shows the distribution in a section through a carbon atom and parallel to the opposite surface of the tetrahedron. We see that the carbon atom has a collar of valence charge; the three-

fold symmetry of which is obvious but not pronounced. In bicyclobutane a similar section through the bridgehead atoms has only two distinct maxima.[7] In the center of the tetrahedron and in the center of its surface plane we find minima which have a relatively high density. The latter is one level unit (0.03 a. u.) lower than the density on the classical valence line between the carbon atoms.

It is obvious that the C–C bonds in tetrahedrane are highly strained. Maksić *et al.*[8] have calculated the hybridization parameters for several strained, cyclic hydrocarbons in their maximum overlap approach. They give the value 29.5° for the angle describing the deviation of the hybrid direction from the C–C interatomic line (for cubane they give the value 11.5°). Baird and Dewar[9] conclude from their SCF-MO calculations that tetrahedrane does not exist as a stable species except under certain conditions at low temperature, and that substituted tetrahedranes should be even less stable than the parent compound. On the other hand, Masamune and Kato[4] find the termal stability of their diphenyl derivative surprisingly high.

The series of hydrocarbons, acetylene, tetrahedrane, cubane, *etc.* which are built up from C–H units is sometimes called "acetylenic" strained hydrocarbons.[10] The valence charge distribution and the general nature of the triple bond do not give reason to include acetylene with the strained single bond compounds. The strained single bonds form a group of bonds by themselves which are richer in energy and more reactive than the unstrained single bond. Perhaps they can be characterized as preexcited or pseudo-excited.

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Studies on Orchidaceae Alkaloids

XXV.* *N*-Isopentenyl Derivatives of Dendroxine and 6-Hydroxydendroxine from *Dendrobium friedricksianum* Lindl. and *Dendrobium hildebrandii* Rolfe

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The quaternary compounds *N*-methyldendrobine[2] (I) and *N*-isopentenyldendrobine[3] (II, one of the possible isomers) have been isolated from *Dendrobium nobile* Lindl. by Inubushi *et al.* In this communication we report the isolation of two quaternary compounds, *N*-isopentenyldendroxine (III) and *N*-isopentenyl-6-hydroxydendroxine (IV), as the chlorides from *D. friedricksianum* Lindl. and *D. hildebrandii* Rolfe. The tertiary bases reported to occur in *D. hildebrandii*,[4] *i.e.* nobilonine,** 6-hydroxynobilonine and dendramine, have also been found in *D. friedricksianum*.

It is evident, from the IR and NMR spectra, that both III and IV, contain an isopentenyl group. Pyrolysis of III and IV at 160° gave dendroxine[6] and 6-hydroxydendroxine,[7] respectively. The facile loss of the isopentenyl groups indicates that they are attached to the quaternary nitrogen atoms. Alkylation of 6-hydroxydendroxine with 1-bromo-3-methyl-2-

* Number XXIV of this series, see Ref. 1.

** We prefer the name nobilonine instead of nobiline, since the latter can be confused with nobilin.[5]