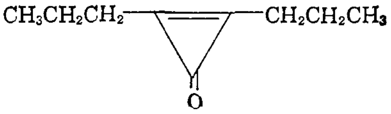
the much more convenient reaction between diphenylacetylene, bromoform, and potassium *t*-butoxide. Although the stability of this ketone seemed to be due to aromaticity of the cyclopropenone system, there was the difficulty that the phenyl substituents might be markedly stabilizing an otherwise unstable ketone, as they do in the cyclopentadienone series. Accordingly we have now prepared a cyclopropenone with simple alkyl substituents, dipropylcyclopropenone, and have studied its stability.



Reaction of dipropylacetylene with dichlorocarbene, either from the decarboxylation of sodium trichloroacetate[3] or better (~ 5% yield) from the reaction between sodium methoxide and ethyl trichloroacetate,[4] yielded dipropylcyclopropenone after isolation by acid extraction (*vide infra*), b.p. 66° (0.3 mm.). *Anal.* Calcd. for $C_9H_{14}O$: C, 78.26; H, 10.15. Found: C, 77.99; H, 10.34. In the infrared the ketone had the strongest absorption at 1850 cm.$^{-1}$, as expected (the diphenyl ketone absorbs at 1865 cm.$^{-1}$, with a shoulder at 1850 cm.$^{-1}$), and in addition it had strong absorption at 1640 cm.$^{-1}$, as observed for the diphenyl ketone. The ultraviolet spectrum showed only end absorption ($\epsilon_{215\ m\mu} = 540$).[5] The n.m.r. spectrum[6] was as expected, showing the characteristic pattern of a propyl group with an electron-withdrawing substituent, with a (four proton) triplet centered at 240 (J, 7 c.p.s.), a (four proton) sextuplet at 293 (J, 7 c.p.s.), and a (six proton) triplet at 334 (J, 7 c.p.s.).

The dipropyl ketone is somewhat more basic than the diphenyl ketone, and with 12 *N* hydrochloric acid it is extracted completely from an equal volume of carbon tetrachloride, and 50% extracted with 6 *N* acid, while the diphenyl ketone is only 50% extracted with 12 *N* acid; the compounds are regenerated unchanged by addition of sodium bicarbonate. Dipropylcyclopropenone is moderately sensitive to oxygen, and indeed satisfactory analytical results could be obtained only when it was handled under nitrogen. However, in other respects it is remarkably stable. Thus after 15 min. at 190° under nitrogen the compound is only 75% destroyed, while the diphenyl ketone is destroyed completely after 5 min. under these conditions, and indeed is 75% destroyed after 15 min. at 160°. Perhaps more striking than this greater thermal stability of the dipropyl ketone is its greater stability toward base. Preliminary studies show that the diphenyl ketone is 90% cleaved after 3 min. at 31° in 0.1 *N* ethanolic sodium hydroxide, the product being stilbenecarboxylic acid, but the dipropyl ketone is recovered completely unchanged after one hour under the same conditions.

These results do not necessarily signify a greater stabilizing effect for the propyl substituents than for the phenyls, but on the contrary they more likely reflect greater stabilization by the phenyl groups of the transition states in the decompositions. It is particularly apparent that the developing anion in the basic ring-cleavage reaction would be strongly stabilized by phenyl groups. However, the properties of dipropylcyclopropenone support the idea that the high stability of these very strained compounds is due to special aromatic conjugation. The obvious extension of this work to other cyclopropenones of interest is currently under way.

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RECEIVED JUNE 29, 1960

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[3] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[4] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

[5] *Cf.* the similar interesting situation in the case of the dipropylcyclopropenium ion, R. Breslow and H. Höver, THIS JOURNAL, **82**, 2644 (1960).

[6] N.m.r. spectrum in CCl_4 solution at 60 megacycles. Shifts relative to an external benzene capillary.

STRUCTURE OF $B_{12}H_{12}^{-2}$ ION

Sir:

The recent isolation[1] of $K_2B_{12}H_{12}$ recalls the molecular orbital predictions of the stability of either the icosahedral[2,3] or the closely related cube-octahedral[4] $B_{12}H_{12}$ arrangements as the −2 ions. An X-ray diffraction study of $K_2B_{12}H_{12}$ has now shown that $B_{12}H_{12}^{-2}$ is very nearly icosahedral in the crystal.

The crystals are cubic in the space group T_h^3–Fm 3, with $a = 10.61$ Å. (standard deviation, $\sigma = 0.01$ Å.), and with 4 molecules in the unit cell. With the origin at the center of the $B_{12}H_{12}^{-2}$ polyhedron (Fig. 1), the 8K atoms are in positions[5] 8(c): $^1/_4\ ^1/_4\ ^1/_4$, etc., and the 48 B are in positions 48(h): $0zy$, etc., with $y = 0.1359$ ($\sigma = 0.0004$) and $z = 0.0827$ ($\sigma = 0.0004$). The 48H atoms are also in positions 48(h) with $y = 0.220$ ($\sigma = 0.005$) and $z = 0.138$ ($\sigma = 0.005$). Weissenberg photographs of levels 1, 3 and 5 about the cube axis yield values of $R = \Sigma\ ||Fo| - |Fc||/\Sigma|Fo| = 0.099$ for the 43 observed reflections to which only B and H contribute. The 75 observed reflections from levels 0, 2, 4 and 6 yield $R = 0.061$ for the complete structure. Corresponding values of $r = \Sigma w(|F_0|^2 - |Fc|^2)^2/\Sigma w|F_0|^4$ are 0.067 for odd levels and 0.047 for even levels, after refinement by least squares procedures.

The space group requires at least T_h-m3 symmetry for the $B_{12}H_{12}^{-2}$ ion, but excludes the four-fold axes of the cube-octahedron. The 6 B–B bond distances along the edges of the cubic cell are 1.755 Å. ($\sigma = 0.007$ Å.), while the 24 B–B distances around the three-fold axes of the polyhedron are 1.780 Å ($\sigma = 0.007$ Å.) as if they are spread slightly by steric interaction between the corresponding H atoms and the K^+ ions. The deviations in the crystal of these two types of B–B distances from their mean distance of 1.77 Å. for a regular icosahedron are so small that it seems reasonable to believe that the isolated $B_{12}H_{12}^{-2}$ ion would indeed have the full icosahedral symmetry. Each K^+ ion is surrounded

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[1] A. R. Pitochelli and M. F. Hawthorne, THIS JOURNAL, to be published.

[2] H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (*London*), **A230**, 110 (1955).

[3] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[4] W. N. Lipscomb and D. Britton, *ibid.*, to be published.

[5] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 311.

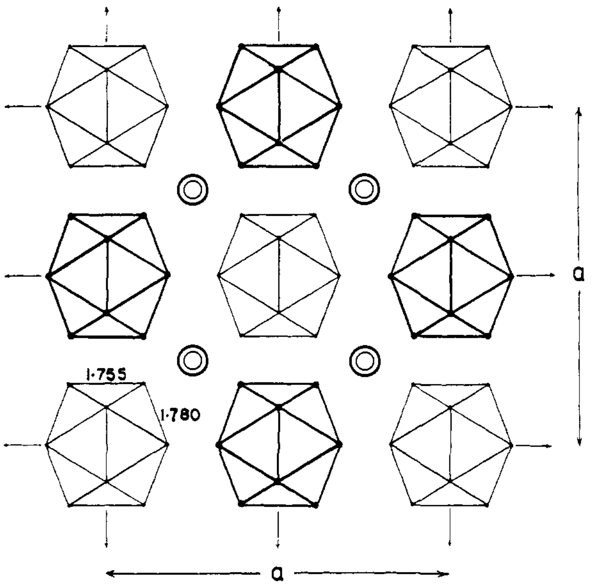

Fig. 1.—The unit cell of $K_2B_{12}H_{12}$, with the center of symmetry at the origin. The icosahedra have been drawn at two-thirds of their proper size in order to avoid overlap. Icosahedra at level zero are indicated by lighter lines, and those at level $^1/_2$ are indicated by heavier lines. Double circles indicate K^+ at levels $^1/_4$ and $^3/_4$.

by 24 H atoms at a distance of 2.29 Å. (σ = 0.06 Å.). The B–H bond length of 1.07 Å. (σ = 0.06 Å.) is short, but just within 3 standard deviations of the average B–H distance of 1.21 Å. found in boron hydrides and their derivatives.[6]

We wish to thank Dr. M. F. Hawthorne for supplying us with the sample, and the National Institutes of Health and the Air Force Office of Scientific Research for financial support.

[6] W. N. Lipscomb, "Advances in Inorganic and Radiochemistry," Vol. 1, Academic Press, New York, N. Y., p. 117.

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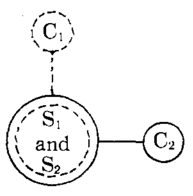
RECEIVED JULY 5, 1960

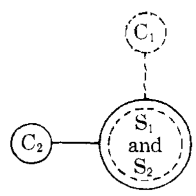
THE ENERGY BARRIER BETWEEN THE ENANTIOMERS OF 1,2-DITHIANE[1]

Sir:

The dihedral angle in an organic disulfide can produce two different molecular conformations, I and II.



I



II

These are optical antipodes, and their stability depends on the height of the rotational barrier hindering free rotation about the disulfide bond. We have studied the interconversion between the enantiomers of 1,2-dithiane by nuclear magnetic resonance. This molecule gives, however, a very complicated n.m.r. spectrum, and therefore we prepared a deuterium-substituted derivative (III).

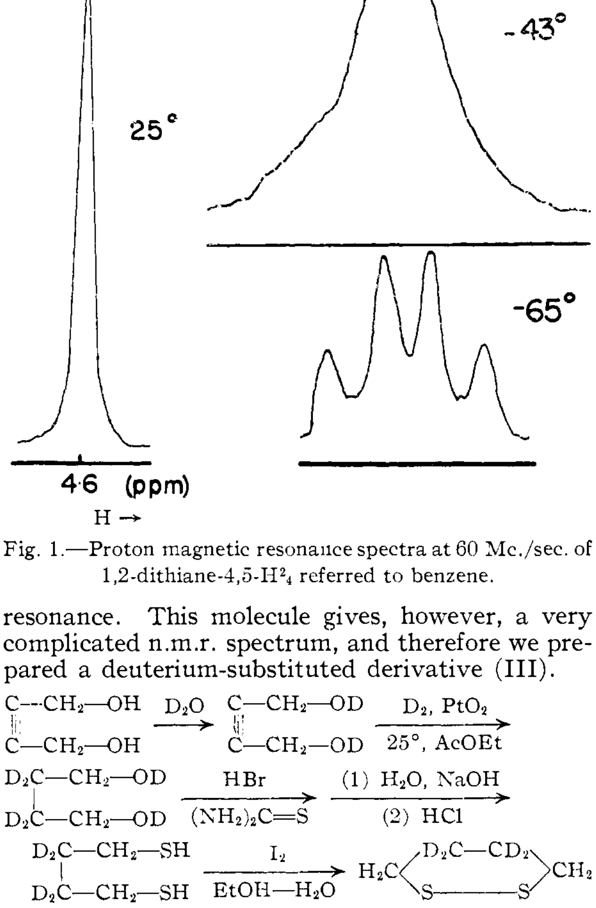


Fig. 1.—Proton magnetic resonance spectra at 60 Mc./sec. of 1,2-dithiane-4,5-H^2_4 referred to benzene.

(III)

From low temperature studies of a 1 *M* solution in carbon disulfide we obtained data which provide an estimate of the rotational barrier for this molecule.[2]

At temperatures below −50° the spectrum consists of a quartet of the AB type[3] (Fig. 1). The maximum separation of the two inner peaks is 10.4 c./sec., and the coupling constant is 13.0 c./sec. When the temperature is raised above −50°, the peaks in the quartet start to converge, and at −43° the spectrum consists of one single broad peak. As the temperature increases above −43°, the peak sharpens and remains constant up to the highest temperature studied (150°).

From the low temperature pattern the chemical shift between the axial and equatorial hydrogens, $\gamma_a - \gamma_e$, was calculated as 18.5 c./sec. We assumed that the following relation for the rate of interconversion[4] holds approximately at −43°, the temperature where the peaks coalesce

$$k = \pi(\nu_a - \nu_e)/\sqrt{2}$$

From this we calculated the rate constant k = 41.1 sec.$^{-1}$.

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[1] The work described in this paper was supported in part by the U.S. Atomic Energy Commission.

[2] A Varian high-resolution n.m.r. spectrometer V-4311, operating at 60 Mc./sec. was used to obtain the spectra.

[3] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N.Y., 1959, p. 119.

[4] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).