to 12% monodehydro[20]annulene (e.g., 3)[8] as purple-brown prisms which decomposed on attempted melting point determination: homogeneous when chromatographed on 0.5% silver nitrate–silica gel; mass spectrum m/e 258.140 (calcd for $^{12}C_{20}{}^{1}H_{18}$ 258.141); $\lambda_{max}^{Et_2O}$ 308 (sh) (ϵ 94,400) and 322 nm (124,000); $\nu_{max}^{CHCl_3}$ 2180 (w), 1000 (s), 980 (s), and 960 (s) cm^{-1}.[9] Catalytic hydrogenation in tetrahydrofuran over platinum gave cycloeicosane (mass spectrum m/e 280).

The nmr spectrum of the monodehydro[20]annulene at $-90°$ (Figure 1) consisted of very complex multiplets at τ -3.3 to -0.1 and 4.0 to 5.7, the integrated areas being $\sim$5:13.[10] The integration shows these bands to be due to the inner and outer protons, respectively, and indicates a "tetra-cis" structure, such as 3. The relative positions of the bands shows the existence of a paramagnetic ring current, as expected of a 20-out-of-plane-π-electron system.[2b] A similar effect has already been observed in the low-temperature nmr spectrum of 1,11-bisdehydro[20]annulene, although in this case "averaging" of the trans double bond protons occurs at room temperature, due to the equivalence of the interconverting forms.[2b]

The partial catalytic hydrogenation of monodehydro[20]annulene was carried out in benzene solution over a 5% palladium/calcium carbonate catalyst, the reaction being terminated when $\sim$2 mol equiv of hydrogen had been absorbed. Chromatography on silica then gave 7% [20]annulene (4), followed by $\sim$35% unchanged monodehydro[20]annulene. [20]Annulene formed brown-red needles (dark red in concentrated solution): mp 139–140° dec (sample placed on block at $\sim$120°); homogeneous when chromatographed on 0.5% silver nitrate–silica gel; mass spectrum m/e 260.156 (calcd for $^{12}C_{20}{}^{1}H_{20}$ 260.157); $\lambda_{max}^{Et_2O}$ 323 nm (ϵ 146,000); $\nu_{max}^{CHCl_3}$ 1000 (s) and 980 (s) cm^{-1}. Catalytic

hydrogenation in tetrahydrofuran over platinum again gave cycloeicosane (mass spectrum m/e 280).

The nmr spectrum of [20]annulene was found to be temperature dependent (Figure 2). At $-105°$, it consisted of a low-field multiplet at τ -3.9 to -0.9 due to the inner protons and a high-field multiplet at τ 3.4–5.9 due to the outer protons; the spectrum is again indicative of a paramagnetic ring current, as expected of a [4n]annulene.[2b] At higher temperatures, these bands broaden and then coalesce (coalescence temperature $\sim$$-60°$). An "average" signal appears above the coalescence temperature, and at 25° this signal consisted of a sharp singlet at τ 2.82. This temperature effect is similar to that of most of the other annulenes investigated.[2b]

The integrated areas of the low-field and high-field bands in the low-temperature nmr spectrum of [20]-annulene were almost exactly 7:13, pointing to a "tri-cis" structure, such as 4. However, the complexity of the spectrum indicates the presence of a stereoisomeric mixture in solution. The value of $\Delta G^{\pm}$ for the barrier to conformational interconversion, calculated as described previously,[11] was 9.2 kcal mol^{-1}.

The nmr spectra of all annulenes from the 6- to the 24-membered ring compounds have now been determined.[2,12] With two exceptions, all the [4n]annulenes show a paramagnetic ring current, and all the [4n + 2]-annulenes a diamagnetic ring current, in agreement with theory. The exceptions are [8]- and [10]annulene, which prove to have no ring current, presumably due to their nonplanarity.

(11) I. C. Calder and P. J. Garratt, J. Chem. Soc. B, 660 (1967).
(12) See R. C. Haddon, V. R. Haddon, and L. M. Jackman, Fortschr. Chem. Forsch., 16, 105 (1971).

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Tricarba-closo-octaborane(7), a Polyhedral Carborane Containing a "Bare" Carbon Atom

Sir:

The importance of isoelectronic sequences among boron compounds implies the existence of polyhedral carboranes containing more than two carbon atoms, which in theory would be generated from members of the known $C_2B_{n-2}H_n$ series by the formal replacement of one or more BH groups with carbon atoms. We wish to report the isolation and characterization of the first such molecule,[1] $C_3B_5H_7$ (I), an isoelectronic analog of the known polyhedral species $C_2B_6H_8$[2,3] and $B_8H_8^{2-}$.[4] Compound I was isolated quite unexpectedly during a

(8) For a preliminary study of the rearrangement of 2 to monodehydro[20]annulene, see F. Sondheimer and Y. Gaoni, J. Amer. Chem. Soc., 83, 1259 (1961).
(9) Occasionally, small quantities of another monodehydro[20]-annulene, with very similar properties, were isolated. However, this isomer was not investigated further.
(10) The nmr spectrum at room temperature was similar, but was less well resolved.

(1) Icosahedral carboranes containing unsubstituted Ge, Sn, or Pb atoms have been reported: R. L. Voorhees and R. W. Rudolph, J. Amer. Chem. Soc., 91, 2173 (1969); R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, ibid., 92, 3351 (1970); L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, ibid., 91, 3376 (1969).
(2) (a) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, Inorg. Chem., 8, 1907 (1969); (b) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, J. Amer. Chem. Soc., 90, 869 (1968).
(3) R. E. Williams and F. J. Gerhart, ibid., 87, 3513 (1965).
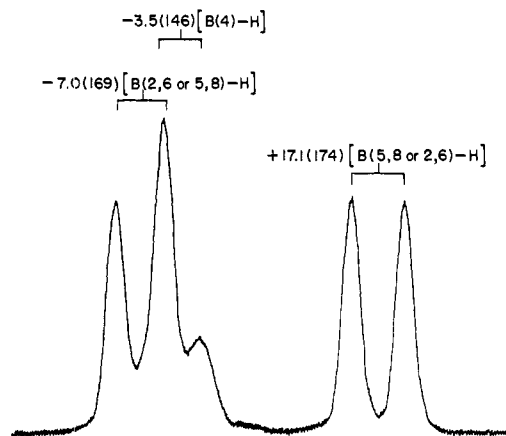(4) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, Inorg. Chem., 6, 1271 (1967).

Figure 1. ¹¹B nmr spectrum (32.2 MHz) of $C_3B_5H_7$ (CS_2 solution). Chemical shifts are in parts per million relative to external $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are in parentheses. Coupling constants for the two overlapped low-field doublets are taken from the proton nmr spectrum.
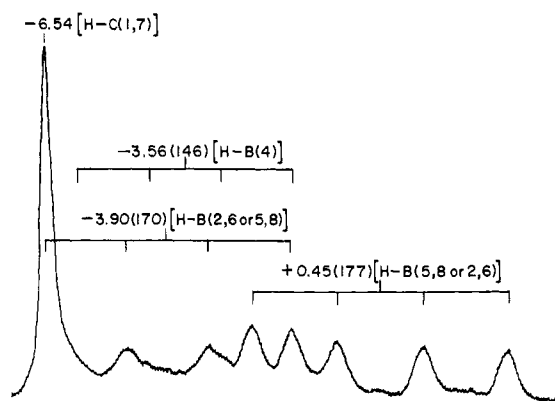

Figure 2. ¹H nmr spectrum (100 MHz) of $C_3B_5H_7$ (CS_2 solution). Chemical shifts are in parts per million relative to external $Si(CH_3)_4$, and coupling constants are in parentheses. The area 2 H–B quartets are clearly apparent, but assignment of the area 1 quartet, expected for the unique boron, is less certain due to masking by the stronger peaks.
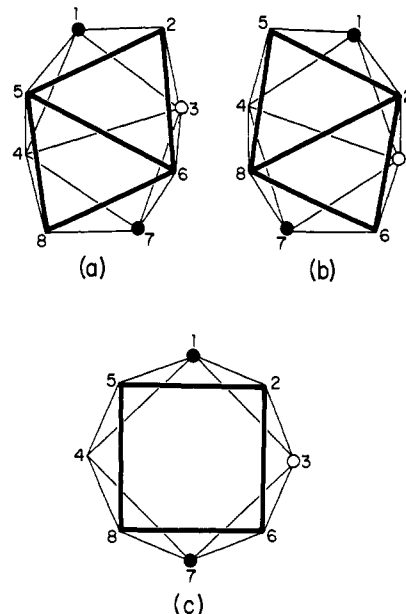

Figure 3. (a and b) Proposed dodecahedral equilibrium structures for $C_3B_5H_7$. (c) Square antiprism time-averaged geometry for $C_3B_5H_7$: ●, CH groups; O, unsubstituted carbon atom; the remaining vertices are occupied by BH groups.

study of silylcarborane rearrangements,[5] from the pyrolysis of μ-silyl- or 4-silyl-2,3-dicarba-$nido$-hexaborane-(8), $SiH_3C_2B_4H_7$. Yields of I in repeated experiments at 220–250° averaged 15–20%. The new carborane is a colorless crystalline solid, mp 37 ± 1°, vp 26.8 ± 0.2 (23°) and 7.8 ± 0.2 Torr (0°), glpc retention volume 2.5 (2,4-$C_2B_5H_7$ = 1) on 30% Apiezon-L–Chromosorb-W at 73°.

Although the conventional electron-impact mass spectrum of I does not contain detectable parent ion peaks (see below), the molecular formula is established by the chemical ionization mass spectrum in methane. The cutoff peak at m/e 99.1089 corresponds to the $C_3B_5H_8^+$ (P + 1) ion (calcd 99.1092), which arises from protonation[6] of the parent $C_3B_5H_7$ species by CH_5^+. The profile in the parent region corresponds closely to that calculated for five boron atoms, and vapor density

measurements of I yield a molecular weight of 97.5 ± 4 (average of five determinations).

The 32.2-MHz ¹¹B nmr spectrum of I (Figure 1) contains three partially overlapped doublets in an approximate 2:2:1 area ratio, indicative of five boron atoms, each bonded to a terminal hydrogen. The 100-MHz ¹H nmr spectrum (Figure 2) exhibits a single H–C resonance and the expected H–B quartets in an H–C/H–B area ratio of approximately 2:5. The gasphase infrared spectrum contains a very strong B–H stretching band at 2620 cm⁻¹, with other significant absorptions at 1304 (m), 1294 (s), 1224 (m), 1033 (vs), 1029 (vs), 900 (s), 896 (sh), 866 (m), 856 (s), 794 (m), 666 (m), 660 (m), 655 (s, sharp), and 643 (m) cm⁻¹.

These data strongly suggest a polyhedral cage structure, particularly in view of the low chemical shift of the H–C proton nmr resonance, the absence of a C–H infrared stretching band (a typical property of small polyhedral carboranes), and the lack of B–H–B bridge absorptions in the ir spectrum. Since each of the isoelectronic analogs $C_2B_6H_8^7$ and $B_8H_8^{2-}$[4] has been shown from X-ray studies to be dodecahedral with near-D_{2d} symmetry, it is reasonable to assume a similar geometry for $C_3B_5H_7$. A rigid D_{2d} polyhedron would not be consistent with the ¹¹B nmr spectrum unless coincidental superposition of nonequivalent B–H resonances were assumed, an unlikely situation in view of the sharp, well-defined B–H doublets. However, if the molecule undergoes rapid cage rearrangement between dodecahedral equilibrium structures as indicated in Figure 3a,b, the nmr spectra may be accounted for in terms of a time-averaged geometry such as the square antiprism shown in Figure 3c. In this arrangement, B(2) and B(6) would be equivalent on the nmr time scale, as would the pairs B(5)–B(8) and C(1)–C(7). The placement of the CH groups at positions 1 and 7 is based on the commonly observed

(5) M. L. Thompson and R. N. Grimes, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR-6.

(6) Protonation of the molecular ion is commonly observed under these conditions (e.g., the cutoff for 2,4-$C_2B_5H_7$ occurs at m/e 87, corresponding to the $C_2B_5H_8^+$ species). For a review of the chemical ionization method, see F. H. Field, Accounts Chem. Res., 1, 42 (1968).

(7) H. Hart and W. N. Lipscomb, Inorg. Chem., 7, 1070 (1968).

tendency for these moieties to occupy nonadjacent positions in carborane polyhedra. Similar arguments have been proposed or considered for the C,C'-dimethyl derivative of $C_2B_6H_8$[2b] and $B_8H_8^{2-}$,[4] both of which have unexpectedly simple ^{11}B nmr spectra.

Compound I is thermally stable to at least 250° and is apparently unreactive with air. However, its conversion to 2,4-$C_2B_5H_7$ [dicarba-*closo*-heptaborane(7)] is strongly favored thermodynamically, as shown in two experiments. In the electron-impact mass spectrometer, I is converted to $C_2B_5H_7$ and no evidence of the original three-carbon species is seen. Secondly, pyrolysis of I at 400° generates $C_2B_5H_7$ in virtually 100% yield.[8] Presumably, the driving force in these processes arises from the considerable thermal stability of the $C_2B_5H_7$ polyhedron, although the presumed presence of an unshared electron pair on $C_3B_5H_7$ is also likely to be a factor contributing to increased reactivity of the molecule.

The synthesis of I from silylcarboranes is difficult to rationalize at this point, although unexpected findings of this kind are not particularly unusual in gas-phase borane reactions. An earlier result which may be related to the present work is the formation of small closo carboranes from dimethylsilane and pentaborane-(9).[9] Such reactions could involve methyne (CH) insertion into the borane cage, but more exotic mechanisms, such as the formation and subsequent disproportionation of unstable closo silacarborane intermediates, are also conceivable. Further studies of the $C_3B_5H_7$ system are in progress and will be reported at a later date.

(8) The fate of the ejected carbon atom has not yet been established, partly owing to the small scale of the pyrolysis experiments. However, no volatile products other than 2,4-$C_2B_5H_7$ have been detected by glpc analysis.

(9) W. A. Ledoux and R. N. Grimes, *J. Organometal. Chem.*, **28**, 37 (1971).

(10) On sabbatical leave from Lake Forest College, Lake Forest, Ill., 1970–1971.

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Polarization of Electronic Transitions in 9-Ethylguanine

Sir:

Knowledge of the electric dipole transition moments of the DNA bases is of interest because they enter, as matrix elements, into theoretical treatments of optical properties and energy transfer in DNA. The transition moment directions for bands between 270 and 230 nm for all the principally occurring DNA and RNA bases have been experimentally assigned except for guanine.[1]

In this communication we wish to report the results of polarized specular reflectance measurements of single crystals of 9-ethylguanine which, in conjunction with

(1) For references, see T. O. Lewis and W. A. Eaton, *J. Amer. Chem. Soc.*, **93**, 2054 (1971).
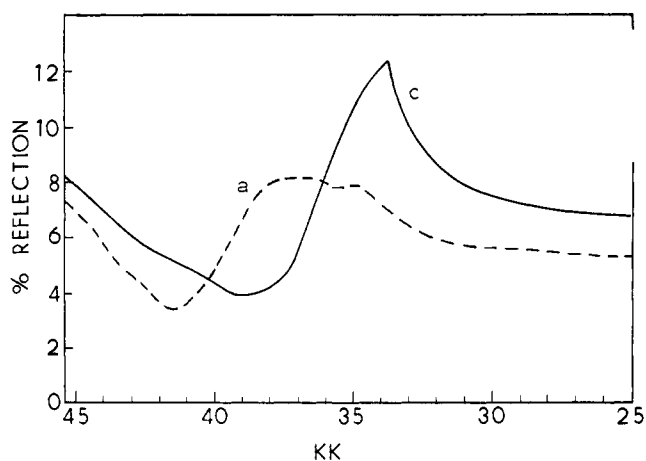

Figure 1. Polarized specular reflectance for the *ac* face of a single crystal of 9-ethylguanine: (———) light polarized along the *c* axis (optic axis), (- - -) light polarized perpendicular to the optic axis.

the recently solved crystal structure,[2] yield information concerning the absolute directions of the transition moments for the first two strong transitions of the guanine chromophore. These two bands have maxima at *ca.* 270 nm (ϵ_{max} ~9000) and 253 (~13,000)[3] and will hereafter be referred to as I and II, respectively.

The crystals of 9-ethylguanine were obtained by slow evaporation of methanol solution at 20°. Experimental details regarding measurement of the reflection spectra are as described previously.[4]

The essential details of the crystal structure are as follows.[2] The crystal system is tetragonal with space group $P_{4_12_12}$. Thus all information regarding electric dipole transition moments is obtainable from measurements on a single face parallel to the *c* axis. It turns out that there are only four electromagnetically distinct molecules per unit cell when viewing the *ac* face. Two of these may be considered as having their planes parallel to *ac* and the other two as having their planes parallel to *bc*. (Actually, all the molecules have their planes tipped 5° away from the *c* axis. Ignoring this does not significantly affect analysis of the data.) The arrangement of the molecules in the crystal is such that a vector drawn between atoms N_2 and C_8 (numbering as in Figure 2) is with in 2° of being perpendicular to the *c* axis (optic axis) for every molecule. It follows that the N_2–C_8 vector is parallel to *a* for half the molecules and parallel to *b* for the other half. It also follows that the in-plane vector perpendicular to N_2–C_8 is within 2° of being parallel to *c* for every molecule.

Turning now to Figure 1, we see the specular reflectance taken on the *ac* face. When the light is polarized along the *c* axis, there is only one "anomaly" in the reflection curve. It is centered at 36 kK (278 nm) and therefore is caused by transition I. Evidently, the transition moment of II is nearly perpendicular to *c* for every molecule and thus lies close to the N_2–C_8 direction.

When the light is polarized along the *a* axis, one indeed sees II manifested strongly by an anomaly centered at 39.5 kK (253 nm). That II does not appear as

(2) R. Destro and R. E. Marsh, manuscript in preparation.

(3) (a) P. R. Callis, E. J. Rosa, and W. T. Simpson, *J. Amer. Chem. Soc.*, **86**, 2292 (1964); (b) L. B. Clark and I. Tinoco, Jr., *ibid.*, **87**, 11 (1965).

(4) P. R. Callis and W. T. Simpson, *ibid.*, **92**, 3593 (1970).