sphere. Weissenberg photographs of levels hkL for $0 \leq L \leq 6$ using Cu Kα radiation and precession photographs of levels Hkl for $0 \leq H \leq 2$ and of levels hKl for $0 \leq K \leq 2$ using Mo Kα radiation were collected. All photographs were taken at low temperature by cooling the crystal with a conventional nitrogen vapor cold stream in order to reduce thermal motion in the crystal and to eliminate a tendency for the sample to sublime at room temperature. The crystal is orthorhombic, space group Pmn2$_1$, $a = 7.21 \pm 0.02$, $b = 9.30 \pm 0.03$, $c = 7.62 \pm 0.02$ A at approximately −135°, with two molecules per unit cell.

The carbon and boron atoms were located with some difficulty from analyses of the Patterson, symmetry minimum,[4] vector verification,[5] and Patterson superposition functions. Difference Fourier maps established all hydrogen atom positions except the methyl hydrogens which appear disordered. Least-squares refinement with isotropic thermal parameters has reached a residual of 0.11 for a structure in which the methyl

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

hydrogens have been omitted.

The bond distances, shown in Table I, are in general agreement with similar bonds in other carboranes.

Table I. Bond Distances

Bond	Distance, A	Bond	Distance, A
B_1–B_3	1.85	B_5–B_{11}	2.05
B_1–B_2	1.79[a]	B_{10}–B_{11}	2.06
B_1–B_4	1.81	C_6–C_6'	1.51
B_1–B_5	1.78	C_9–C_9'	1.53
B_1–B_{10}	1.78	C_6–B_{11}	1.68
B_2–B_5	1.81	C_9–B_{11}	1.66
B_4–B_{10}	1.83	B_1–H_1	1.15
B_2–C_6	1.70	B_2–H_2	0.97
B_4–C_9	1.70	B_4–H_4	0.94
B_5–B_{10}	1.87	B_5–H_5	1.20
B_5–C_6	1.59	B_{10}–H_{10}	0.96
B_{10}–C_9	1.60	B_{11}–H_{11}	1.25

[a] Distances for the half-molecule within the crystallographic asymmetric unit are given. The bonds in brackets are related by a molecular plane of symmetry not required by crystal symmetry. The estimated errors are ±0.01 A for C–C, B–C, and B–B, and ±0.11 A for B–H.

The molecule has mm-C$_{2v}$ symmetry. Crystal symmetry requires the molecule to have at least m-C$_s$ symmetry (the molecular plane containing atoms B_2, B_4, C_6, C_9, and B_{11} in Figure 1), and a second plane, the perpendicular bisector of a C_6–C_9 vector, is apparent from the bond lengths. The molecule resembles $B_{10}H_{12}(CH_3CN)_2$[6] and $B_{10}H_{12}(S(CH_3)_2)_2$[7] in geometrical and valence structures. The most notable difference is a shortening of the 6–9 interatomic distance due to bonding with the apical B_{11} atom and the fact that some B–B bonds have been replaced with shorter B–C bonds. We observe a 6–9 distance of 3.09 A as compared with 3.32 A in $B_{10}H_{12}(CH_3CN)_2$, 3.21 A in $B_{10}H_{12}(S(CH_3)_2)_2$, and a much longer 3.55 A in decaborane.[8,9] Perhaps a more discriminating comparison is seen in the ratio of the parallel distances, B_2–B_4/B_6–B_9, which is nearly constant in the three compounds above (0.833, 0.865, and 0.858 respectively) whereas in $B_9C_2H_9(CH_3)_2$ the corresponding B_2–B_4 and C_6–C_9 distances are nearly equal with a ratio of 0.969.

The results of refinement with anisotropic thermal parameters, an approximation for the disordered methyl hydrogens, and other more complete details will be reported later.

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Electron Spin Resonance Study of Mono- and Dimeric Cations of Aromatic Hydrocarbons[1]

Sir:

Lewis and Singer[2] recently investigated the electron spin resonance spectra of cation radicals formed by oxidation with antimony pentachloride of a variety of aromatic hydrocarbons dissolved in methylene chloride. Of particular interest was the observation of a spectrum from naphthalene that appeared to be caused by two sets of eight equivalent protons, each having approximately one-half the hyperfine splitting constant of the naphthalene negative ion radical, which these investigators assigned to a singly charged positive ion dimer. With a slight modification of the techniques, including the use of a concentration gradient in the sample tube,[3] we have confirmed this as well as some of their other results and at the same time have obtained well-resolved spectra from compounds for which spectra were previously either poorly resolved or not observed at all.

The cation dimer formed by naphthalene is not an isolated result. We have found spectra attributable to singly charged dimers on oxidation of both 2,3,6,7-tetramethylnaphthalene and anthracene when an excess of the hydrocarbon is present. In the latter case, a black paramagnetic precipitate is formed at −100° (perhaps the tetrachloroantimonate salt of the hydrocarbon ion). At −85° enough of this dissolves to form a green solution whose spectrum consists of a pattern of narrow lines attributable to the monopositive ion dimer superimposed onto a central asymmetric line about 1 gauss wide resulting from the solid. The green solution is unstable, decaying into a blue, diamagnetic solution, but an approximately steady-

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Table I. Hyperfine Splitting Constants

Radical	Method of Preparation	Ref	Hyperfine splitting a_1^{H}	a_2^{H}	a_9^{H}	Line width[a]
Anthracene$^+$	$SbCl_5$–CH_2Cl_2	*b*	3.079	1.379	6.505	0.055
Anthracene$^+$	$SbCl_5$–CH_2Cl_2	*c*	3.08	1.38	6.49	
Anthracene$^+$	H_2SO_4	*d*	3.061	1.379	6.533	
(Anthracene)$_2^+$	$SbCl_5$–CH_2Cl_2	*b*	1.422 (2.844)[e]	0.710 (1.420)[e]	3.253 (6.506)[e]	0.120
Anthracene$^-$	Na–DME	*d*	2.740	1.509	5.337	
(Naphthalene)$_2^+$	$SbCl_5$–CH_2Cl_2	*b*	2.756 (5.512)[e]	1.032 (2.064)[e]		0.110
(Naphthalene)$_2^+$	$SbCl_5$–CH_2Cl_2	*c*	2.77 (5.54)[e]	1.03 (2.06)[e]		
Naphthalene$^-$	Na–DME	*f*	4.940	1.825		
(2,3,6,7-Tetramethylnaphthalene)$_2^+$	$SbCl_5$–CH_2Cl_2	*b*	2.785 (5.570)[e]	1.144[g] (2.288)[e,g]		0.050
2,3,6,7-Tetramethylnaphthalene$^-$	Na–DME	*h*	4.62	1.62[g]		

[a] The line width is given as the separation in gauss between the extrema of the first derivative spectrum. [b] Data obtained in the present work. Except for the anthracene dimer, the radicals were made with an excess of $SbCl_5$ such that further addition of $SbCl_5$ had no effect on the reaction product. The anthracene dimer was made with an excess of anthracene. [c] From the work cited in ref 2. [d] From the work cited in ref 5. [e] Twice the observed splitting, for comparison with monomer results. [f] R. G. Lawler, J. R. Bolton, M. Karplus, and G. K. Fraenkel, to be published. [g] Methyl proton splitting. [h] J. R. Bolton, Thesis, Cambridge University, 1963.

state radical concentration is obtained because the solid redissolves.

The hyperfine splittings are presented, along with other data for comparison, in Table I. Our results were obtained at approximately −85° and have standard deviations of about ±0.002 gauss. Although to a first approximation the pairing theorem holds and corresponding splittings in the positive ion and negative ion radicals of the same hydrocarbon[3,4] are the same, there are in fact significant deviations, and at most of the positions the splittings are larger in the postive ion than in the corresponding negative ion. This trend has been studied by Colpa and Bolton,[5,6] who propose that the splittings at a position with spin density ρ and charge ϵ should be given by the relation $|a^{\mathrm{H}}| = |\rho|(A + B\epsilon)$. Our results for the ring proton splittings at position 1 fit this relation reasonably well if we make the assumption, justified by the anthracene results, that dimerization does not cause a significant change of relative spin densities at the ring positions. A similar but larger charge dependence for the methyl proton splittings is in accord with the results found for some methyl-substituted anthracene anions and cations.[7] It is of interest that although most of the data for the ring proton splittings at position 2 in hydrocarbon ions are in poor accord with the Colpa–Bolton relation, the results for naphthalene are in reasonable agreement.

These results imply that no major molecular distortion or redistribution of π-electrons occurs on dimerization, and it therefore seems likely that the two hydrocarbon moieties lie in parallel planes. The interaction between two neutral hydrocarbon molecules in parallel planes and with parallel long axes has been studied by Forster and Kasper[8] to explain excimer spectra and by Ron and Schnepp[9] in an investigation of paracyclophanes. It is possible to explain the bonding of the dimers in terms of a simple resonance-integral type of interaction between the 2p orbitals in the two halves, but a similar stabilization is also predicted by a first-order theory for the anion dimers. We have attempted unsuccessfully to produce a negative monoanion dimer of naphthalene by treating a small amount of metallic potassium with an excess of naphthalene in dimethoxyethane; only the usual (but broadened) monomer spectrum was obtained. We are at present attempting to determine whether the tetrachloroantimonate anion plays a significant role in the dimerization.

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The Use of ^{13}C-Labeled Acetate in Biosynthetic Studies[1]

Sir:

The use of ^{14}C-labeled substrates to test and verify proposed biosynthetic pathways has led to the rapid advance of knowledge in this field. The initial concept that the head-to-tail linkage of acetic acid units accounts for the biogenesis of phenolic materials was advanced by Collie,[2] and the idea was further extended and biochemically tested by Birch.[3]

The radioactive tracer technique employing ^{14}C-labeled acetate was employed by Birch in the study of the biogenesis of fungal metabolites derived *via* the polyacetate route with significant results. The degradative reactions necessary for removing the radioactive ^{14}C label from the metabolites included the Kuhn–Roth oxidation for isolating C–CH_3 groups as acetic acid. Labeled carbon atoms in phenolic rings

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