also observed that $\cdot O_2^-$ adds to $Co(bpy)_2^{2+}$ ($k = 1.9 \times 10^6$ $M^{-1}\,s^{-1}$). However, no reaction was observed between $\cdot O_2^-$ and Co^{III}(1,3,8,10-tetraeneN$_4$) or Cu^{II}(4,11-dieneN$_4$)[16] ($k < 10^5\ M^{-1}\,s^{-1}$).

The observation that $\cdot O_2^-$ adds irreversibly to certain metal complexes requires that this reaction be included when consideration is given to the role of $\cdot O_2^-$ in the damage of biological systems. Observation of growth of obligate anaerobes, which do not contain SOD, under aerobic conditions[17] in the presence of added Co^{2+} appears to suggest the possible interaction of $\cdot O_2^-$ and cellular Co(II) complexes. Consideration should be given to the possibility of reaction of $\cdot O_2^-$ and vitamin B_{12} precursors which can lead to severe deficiency of B_{12} triggered by disorders in SOD levels.

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The Structure of 1-Bromo-1*H*-cyclobuta[*de*]naphthalene

Sir:

Recently the syntheses of the peri-bridged compounds 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**1**) and 1*H*-cyclobuta[*de*]naphthalene (**2**) were reported, and their structures assigned, primarily by NMR and intuitive methods.[1] From the magnetic equivalence of its C(1) protons, **2** was surmised to be planar or to rapidly interconvert between equivalent conformers folded along C(8)-C(9).[1] We report here the crystal structure and some revealing chemistry of **1**.

Table I. Bond Distances (Å) and Angles (deg) of Interest[a]

	1[a]	Naphthalene
C(1a)-C(2)	1.356 (6)	1.361 (4)
C(2)-C(3)	1.432 (6)	1.421 (4)
C(3)-C(4)	1.381 (6)	1.361 (4)
C(4)-C(9)	1.420 (7)	1.425 (4)
C(9)-C(8)	1.382 (6)	1.410 (4)
C(1a)-C(8)	1.368 (6)	1.435 (4)
C(8)-C(1a)-C(2)	118.4 (6)	120.2 (2)
C(1a)-C(2)-C(3)	114.6 (6)	120.5 (2)
C(2)-C(3)-C(4)	124.4 (6)	120.5 (2)
C(3)-C(4)-C(9)	120.2 (6)	120.2 (2)
C(4)-C(9)-C(8)	111.1 (6)	119.2 (2)
C(9)-C(8)-C(1a)	130.7 (6)	119.2 (2)
C(4)-C(9)-C(5)	137.7 (6)	121.5 (2)
C(1a)-C(8)-C(7a)	98.7 (6)	121.5 (2)

[a] Values for chemically equivalent bonds and interbond angles have been averaged.

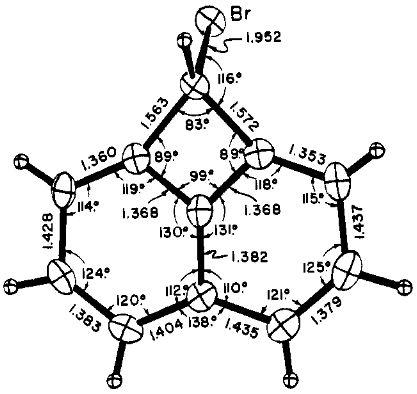
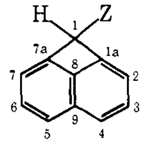


Figure 1. ORTEP diagram of the 1-bromo-1*H*-cyclobuta[*de*]naphthalene molecule. Hydrogen atoms have been reduced in size for clarity. The thermal ellipsoids are shown at the 50% probability level.



1, Z = Br 3a, Z = $O_3SC_6H_4CH_3$-*p*
2, Z = H 3b, Z = O_2CCH_3

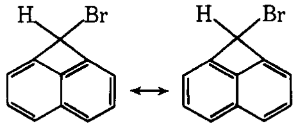
Long colorless transparent needles of **1**, grown from toluene solution, were sealed in capillary tubes and used for cell constant[2] and space group determination[2] and for x-ray diffraction data collection, all at −60 (±5) °C. Intensity data were collected on an automated four-circle diffractometer using graphite monochromatized Mo Kα radiation. The data were corrected for absorption,[2,3] Lorentz-polarization effects and crystal decay, yielding 1717 independent *F*'s (of which 1447 were $>3\sigma$). The structure was solved by the heavy atom Patterson method and refined by standard techniques.[4] Hydrogen atoms were located using difference Fourier maps and their parameters were also refined. The *R* factor is 0.065 and the "goodness-of-fit" is 3.7.[4] All but one pair of chemically equivalent bond distances in the molecule are equal within about one standard deviation.[5]

Table I compares the dimensions of **1** and naphthalene.[6]

Bromide **1** is, surprisingly, essentially planar (Figure 1a) with the angle between the planes defined by the two six-membered rings being about 1.3° (3) and the bromine atom lying on the "concave" side of the molecule. The buckling of the molecule is only barely significant and it is at this point unclear whether the nonplanarity is actually real or simply a minor artifact due to the remaining absorption errors.[5] The thermal motion (Figure 1) does not indicate any abnormal flexing or disorder in the crystal.

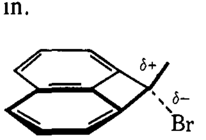
The most striking features of **1** are the changes in the bonding parameters in the naphthalene system on being peri-bridged. The bonds to the bromomethano bridge, which might be expected to be unusually long, are only ca. 0.03 Å longer than a normal carbon-carbon single bond, and their lengths are similar to those in planar cyclobutanes.[7] The strain due to the bridging of the peri-positions is not concentrated solely in the C(1)-C(1a) and C(1)-C(7a) bridge bonds, but rather is expressed by adjustments (particularly in interbond angles), throughout the molecule. This finding accounts for the unexpected thermal stabilities of **1** and **2** and their derivatives.

The net effect of bridging the peri positions has been to compress that portion of the naphthalene nucleus directly connected to the bridge and to cause the opposite side of the molecule to be expanded. In particular, the C(1a)-C(8)-C(7a) angle is compressed to 99°, all of the bonds to C(8) are substantially shorter than in naphthalene, and the C(4)-C(9)-C(5) angle is opened to 138°. The hybridizations of the valence orbitals of C(1), C(8), and C(9) are the most seriously affected of any in **1**. It is tempting to ascribe the variation in the bond distances in the ring to a greater resonance contribution of **1** to the structure than of **5**. From the somewhat greater bond lengths about C(4) and C(5) than about C(2) and C(7) we infer greater p character in the bonds of the former and predict that in **2** electrophilic substitution will occur very selectively at C(4) and C(5).

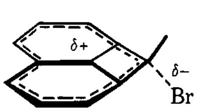


5

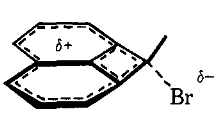
Silver tosylate and silver acetate convert **1** efficiently in hexamethylphosphoramide (75 °C) to **3a** and **3b**, respectively.[8] Of note is that tosylate **3a** solvolyzes slowly in acetic acid at 75 °C (18% in 120 h)[9a] whereas at 25 °C acetic acid converts 9-fluorenyl tosylate rapidly (53% in 5.2 min)[9b] and benzhydryl tosylate (too fast to measure)[9c] to their acetates. Further, sodium azide in hexamethylphosphoramide reacts slower with **1** than with 9-bromofluorene.[10] Displacement of the bromine atom from **1** will be retarded because of the small C(1a)-C(1)-C(7a) bond angle available to its S_N1 (**6a-c**) and S_N2 transition states. What are not yet clear are the extents of the outer ring delocalization (**6b**) in these systems and the complications of the 1,3-cyclobutadiene components (**6c**) therein.



6a



6b



6c

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(5) The full details of the structures of **1** and derivatives will be published by M. Gessner and G. G. Christoph.

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(8) Products **3a–b** are of proper analyses, exact masses, and NMR spectra: **3a**, mp 115.5–117.5 °C; **3b**, bp 86 °C (0.15 mm); picrate, mp 113–115 °C.

(9) (a) Reaction is only 87.5% complete after 650 h at 75 °C. (b) G. W. Corwell, T. D. George, A. Ledwith, and D. G. Morris, *J. Chem. Soc. B*, (1169 (1966). (c) G. W. Corwell, A. Ledwith, and D. G. Morris, *ibid.*, 700 (1967). (d) Additions of 9-bromofluorene and benzhydryl bromide, respectively, to ethanolic silver nitrate give total silver bromide precipitates instantaneously; under these conditions, **2** gives a *trace* silver bromide test in 5 min.

(10) Bromide **1** is 49% converted to the azide by sodium azide in hexamethylphosphoramide at 25 °C in 20 min; in a comparable experiment, reaction of 9-bromofluorene is 100% complete in <4 min.

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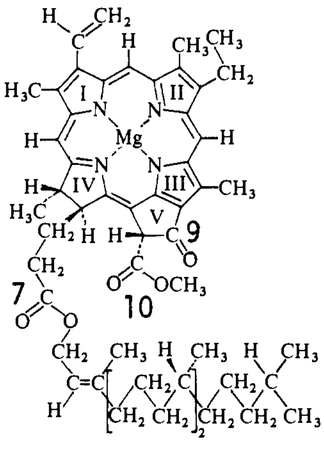
Endo and Exo Carbomethoxy Carbonyl Bonding in Hydrated Chlorophyll a Dimers. Experimental Criteria for the Determination of the P700 Structure in Photosynthesis[1]

Sir:

There exists the belief that the photosystem I reaction center dimer P700 is a C_2 symmetrical dimer of chlorophyll a monohydrate (Chl a·$H_2O)_2$.[2-4] However, two slightly different models have been proposed. Both have been established on experimental grounds.[3,4] The difference lies in the choice of the C9 keto carbonyl[4] or the C10 carbomethoxy group[2,3] as being responsible for the reciprocal C=O···H(H)O···Mg interactions that interlink the monomeric Chl a units in P700. In this communication, we describe the various physical conditions under which both models can exist as stable equilibrium structures and delineate the experimental criteria for identifying the configuration of the in vivo P700 adduct.



The presence of the C9 keto and C10 carbomethoxy carbonyls in ring V and the C7 propionic ester carbonyl in ring IV of the chlorophyll a molecule gives rise to several possible self-aggregating interactions between monomeric units of